Primary Products

Diesel Oil

The analytical data for Ruhrchemie Diesel Oil (as prepared in 1938) are given in Table 51.

Table 51

Ruhrchemie Diesel Oil, 1938

Colour	Pale Yellow
sp.gr. @ 15°C.	0.765
" " " 20°C.	0.762
Acid number	0.02
Flash Point	
Pensky-Martin	75°C.
Open dish	85°C.
Setting point	- 9°C.
C.V., gross	10,900 kg. - cal.
" net	10,100 " "
Viscosity @ 20°C.	1.16°E.
" " 50°C.	1.0°E.
Ash, Water, Asphalt	0%
Analysis	
Carbon	84.8%
Hydrogen	15.2%
O, N, S	0.0%
Boiling range (Engler)	
I.B.P.	200°C.
Up to 225°C.	34%
" " 250°C.	63%
" " 275°C.	82%
" " 300°C.	95%
" " 310°C.	97%
Cetane No.	
(HWA Motor)	ca.85

In recent years, the Diesel oil has conformed to the specification given in Table 52.

Table 52

Ruhrchemie Diesel Oil. Recent Specification

Boiling range	165 - 255°C.
sp.gr.	0.745
Flash point	over 57°C.
Setting point	below -38°C.
Cetane No.	over 70

Dr. Nöbel, of the Homberg Works of Rheinpreussen, was questioned concerning the method of preparing stable mixed Diesel oils from tar oils and Fischer-Tropsch oils, and gave the following information.

The 180-300°C. fraction of coke-oven tar, brown-coal tar or low-temperature tar was mixed with the kogasin, b.p. 160-170° to 230-250°C., in a tank fitted with a high-speed stirrer, and the mixture treated with an electrolyte - the usual one being 20% sulphuric acid. The mixture was allowed to settle and the clear upper layer of oil run off from the sludge. The clear oil was then treated with bleaching earth (Floridin) and washed with 20% caustic soda solution. The electrolyte causes coagulation and precipitation of resinous high-boiling phenols and the alkali treatment removes the crystalline phenols. About 15 to 20 per cent of weight of the original tar oil is lost in this refining treatment.

The high-speed mixed Diesel oil sold by Rheinpreussen contained 40-50%, by weight, of refined tar oil and had the properties given in Table 53.

Table 53

Rheinpreussen Mixed High-Speed Diesel Oil

Cetane No.	75
Octane No.	90 - 100
Setting point	ca.- 25°C.
sp.gr.	0.88 - 0.90
Conradson Carbon	0.02
"Ausflockungspunkt"	- 15°C.
(Appearance of solid matter)	or less

The oil remained perfectly clear after many months storage.

This oil gives a very clean exhaust and only a small proportion of carbon monoxide and was found preferable, on this account, to natural oils for use in underground motors.

For use in low-speed engines, up to 70 or 80% of refined tar oil could be used to give a mixed oil of cetane number 60. The properties of mixed oils prepared using the wider Fischer-Tropsch fraction 180 to 320°C. were less favourable, particularly as regards setting point. (See C.I.O.S. Report, Item No. 30, File No. XXV - 6).

Use of Kogasin as Metal-working Lubricant

Of the 970 t. per month of the 220 - 320°C. 'Kogasin' fraction produced by Hoesch-Benzin, 500 - 600 t. were used, after washing with alkali and drying, as a lubricant for metal cutting, drilling, grinding and polishing. Part was used in the Hoesch steel works and part sold to outside users.

The remainder of the kogasin was sold to Ruhrchemie as cracking stock for lubricating oil synthesis.

Recovery of Fatty Acids and Alcohols

The primary products (more particularly those from the medium-pressure process) always contain small amounts of fatty acids and alcohols, but it was only at the works of Hoesch-Benzin that they were regularly recovered. The procedure was as follows:-

The hot gases from the reaction vessels were neutralised with soda solution at 150°C. The gases entered the bottom of the neutraliser column and the bulk of the soda at the top, but owing to the rapid formation of sodium bicarbonate from the CO_2 present in the gases, it is also necessary to add a portion of the soda in the middle of the column. About 90% of the fatty acids present were removed at this stage and the remainder were obtained by subjecting the Diesel oil fraction of the product to alkali washing.

The fatty acids were recovered by treating the liquors from both processes with sulphuric acid and extracting the liberated acids with benzene.

The approximate composition of the acids is given in Table 54.

Table 54

Primary Fatty Acids. Hoesch-Benzin

$C_2 - C_4$	ca. 30%
$C_5 - C_9$	" 30%
$C_{10} - C_{20}$	" 35%
Residue	" 5%

The monthly production amounted to about 18 t. (or 0.4% of the total primary products of the plant) and the approximate cost of recovery, including capital charges, was given as 100 RM./t. The acids were used mainly in the form of calcium or sodium salts in the company's own grease-making plant.

The alcohols were recovered from the reaction water which separated from the oil after the main condensers, and also from the condensed water obtained when the active carbon scrubbers were being steamed. The combined aqueous liquors, containing 0.5% by weight of alcohols , were distilled to give a distillate containing 70% organic matter, 8-10% of which was aldehydes, ketones, esters etc. and the remainder a mixture of alcohols of the approximate composition given in Table 55.

Table 55

Alcohols from Reaction Water. Hoesch-Benzin

Methyl alcohol	10%
Ethyl "	25%
Propyl "	30%
Butyl "	25%
Amyl and Hexyl alcohols	10%

The crude 70% concentrate was sold to the Reichsmonopol for 1,000 RM./t. pure alcohols. The cost of producing this concentrate was given as 107 RM./t. pure alcohols, which figure includes 7 RM./t. capital charges. The production amounted to 26 t, pure alcohols per month or 0.6% of the total primary products.

No attempts was made to recover higher alcohols from the Diesel oil fraction.

Wax

In the wax refining plant of Ruhrchemie, the residue, b.p. $> 320^{\circ}C.$, from the distillation of the atmospheric-pressure synthesis product, together with the wax recovered

from the catalyst by solvent extraction, was subjected to vacuum distillation at 6 mm. pressure in a still comprising two continuously operated columns, arranged in series. These columns were arranged with the heating coil in an upper compartment and the heat exchanger and condenser in the lower section. The heating was effected by a superheated water circulation. The first column, which provided distillate-I, was maintained at 160°C. and the second, which gave distillate-II and residue, at 280°C. The two distillates were run without further treatment to the "soft wax" storage and the residue after cooling and flaking became 'catalyst wax'.

The residue above 320°C. from the medium-pressure product was subjected to vacuum distillation in a similar pair of columns to give two distillates (130°C. and 300°C.) and a residue. The distillates were neutralised in a disintegrator with 1% of a hot 5% caustic soda solution and then washed with water. The neutralised distillates were then treated in a Henderson sweating plant. Distillate-I gave an oil-free soft wax, m.p. 40 - 45°, 70 parts of which were blended with 30 parts of the hard-wax residue from the distillation, m.p. 90 - 95°C., to give crude "plastic wax", m.p. 75°C. Distillate-II was sweated to give crude 'block paraffin', m.p. 50 - 52°C. The low-melting material from the sweaters went to the combined soft wax storage. The block paraffin, plastic wax and the remainder of the high-melting distillation residue were each refined with 2 to 3% of a mixture of nine parts of "Bleichton 2 Hochativ" (a bleaching earth sold by Bleichton G.m.b.H., München) and one part of "Decolit" (active carbon sold by Lurgi).

The daily input of raw material to the plant was 43,000 kg. (21,500 kg. of normal-pressure residue above 320°C. and 21,500 kg. of medium-pressure residue above 340°C.) and the daily output of refined products was as shown in Table 56.

Table 56.

Daily Output of Refined Wax Products. Ruhrchemie

	Melting point (approximate), °C.	Production kg./day
Soft wax (incl. sweat oil)	35 - 45	22359
Block paraffin	50 - 52	2200
Plastic wax	70 - 75	2688
Catalyst wax	80 - 90	6360
R.B. Hard wax	90 - 95	8976

Flow-sheets for the refining plant are shown in Figures 7 and 8.

Figure 7 also gives the dimensions and other details of the sweating plant, presses and other items of plant.

In the preparation of block paraffin, the sweating process occupied about 48 hours, and the highest melting portion of the sweat oil (about 1/5th of the input to the sweaters) was recirculated with fresh feed. In the early days, de-oiling with solvents had been investigated but it was concluded that sweating was cheaper.

The bulk of the soft wax called "Gatsch", was delivered to Witten for fatty acid manufacture, the remainder, including all the first runnings from the sweaters was cracked to provide raw material for lubricating oil synthesis.

Prior to 1939, Ruhrchemie used the names "Paraffin V" to signify catalyst wax refined by earth treatment, and "Paraffin V.D." for refined hard wax from the medium pressure process. This terminology has not been used since that date.

At Hoesch-Benzin, the residue above 320°C. of their medium-pressure product was vacuum distilled and the fraction below 450°C. (760 mm.) was delivered to Witten and the residue (>450°C. @ 760 mm.) sent to Ruhrchemie, together with the catalyst wax, and refined in the Ruhrchemie plant as described above.

Referring to the Brabag waxes, Dr. Sauter said that the term "Macroparaffin" (which frequently occurs in documents)

was applied both to the total catalyst wax, m.p. ca. 90°C., obtained at the Brabag (Schwarzheide) atmospheric-pressure plant, and to the residue, b.p. > 490°C., m.p. 95 - 100°C., obtained by vacuum steam-distillation of the catalyst wax. The forerunnings, b.p. below 450°C., from the distillation were added to the 'gatsch' and the fraction 450 - 490°C., known as "Medium paraffin", m.p. 40 - 50°C., was used for polishes.

Brabag prepared an ointment base by hydrogenating the crude Macroparaffin at 430°C. and 80 atm. The product, m.p. 45°C., was extracted with pentane and the extract (70% of the input material), after treatment with bleaching earth, was obtained as a soft, white non-viscous product resembling lard. It was rendered odourless by distilling-off lower fractions in steam under reduced pressure. The 30% of material left as residue from the pentane extraction was returned to the bulk Macroparaffin stock.

Dr. Sauter considered that cracking in the presence of hydrogen at 350°C. and 80 atm. was the best method of converting hard wax into gatsch suitable for fatty acid synthesis by the Witten process.

Ruhrchemie consider that the waxes contain about 10 - 20% iso-hydrocarbons with short side chains. They had not carried out any trials of the I.G. modification of the Schaarschmidt $SbCl_5$ method and were inclined to accept the I.G. figures with reserve. From examination of the structure of the olefines present in the primary products (see p. 153), there was some evidence that the proportion of iso-hydrocarbons might be as high as 20 - 40% in the wax fraction, 10 - 20% in the Diesel oil and 5 - 10% in the benzine.

The soft wax has always been considered to be more 'branched' than the hard wax, but Ruhrchemie believe that this may not be so, as the short side chains will affect the physical properties less, the longer the main chain. This is particularly the case with α-methyl groups.

Ruhrchemie gave the following general information concerning the utilization of the grades of wax sold by them.

'Soft Wax' was used as cracking stock, as raw material for the Witten oxidation process, for the impregnation of paper and matches, for the manufacture of leather oils, and

in the artificial flower industry.

'Block Paraffin' was a substitute for the similar material derived from petroleum and brown-coal tar.

'Plastic Wax' was used for the impregnation of wooden or cardboard casks, in the manufacture of paper and artificial flowers, in the manufacture of ointment bases, leather preserving products and candles.

'Refined Hard Wax' was used in the impregnation of paper, textiles, wooden barrels, in the manufacture of candles, floor and boot polish, leather preserving products, lubricants, carbon papers, for electrical insulating materials, particularly in condensers, rust protection of metal, electrolytic bath covering and in the artificial flower industry.

The principal firms to whom deliveries of these waxes were made by Ruhrchemie were as follows:-

Ceresin Plants	Other Industries
Schliemann, Hamburg.	Sidol-Werke, Köln.
Schlickum, Darmstadt.	Chemische Fabrik Pferson, Augsberg.
Struve, Hamburg.	Thompson-Werke and Jagenbergwerke, Düsseldorf
Prüser, Hamburg.	Ludwig Müller, Heilbronn.
Lüneburger Wachswerke, Lüneburg.	Hydra-werk, Berlin.
Vogelsang-Werke, Hamburg.	
Compes, Düsseldorf.	The following carbon-paper manufacturers:-
Tromm, Köln.	
Schütz, Frankfurt a. M.	
Berliner Ceresinfabrik, Berlin-Neukölln.	
Chemische Fabrik Dessau, Dessau.	Günther Wagner
	Geha-Werke

Ruhrchemie stated that the ceresin manufacturers made blends of Fischer-Tropsch wax with residual wax from petroleum distillation as substitutes for ozokerite.

Removal of Alcohols, etc.

The alcohols and other oxygen-containing substances which occur in the primary products of synthesis with iron catalysts can be separated from the hydrocarbons by counter-current extraction with a 20% aqueous solution of soap. The alcohols can then be removed from the soap solution by

extracting it with benzene.

Ruhrchemie had also been successful on the laboratory scale with chromatographic methods using silica gel, aluminium silicates or activated alumina. The primary product was passed through three columns in series at slightly reduced pressure and the effluent from the third column was practically free from oxygen compounds. The alcohol concentrate could be displaced from the absorbent by hot or cold water.

Refining of Primary Products for Lubricating Oil Synthesis

For the production of lubricating oil by polymerisation of the olefines present in the primary product, it is necessary to remove alcohols and other compounds which react with aluminium chloride. Ruhrchemie had developed two processes for this purpose. In one process, the feed-stock was vapourised and passed over activated alumina at 350°C. at a rate of 100 - 200 ml. liquid per 100 ml. catalyst per hour. After 400 hours it was necessary to interrupt the process to burn off carbonaceous deposits on the catalyst, but after 1,000 hours the catalyst was still active. The loss obtained in laboratory trials was not more than 0.2 to 0.3%. It was claimed that no shifting of the double bond of α-olefines occurs during the process, the main reaction being the dehydration of alcohols.

The other process consisted in treating the feed-stock in the liquid phase with concentrated $ZnCl_2$ solution at 140 - 160°C., in counter-current. This process was just as effective as the other and somewhat cheaper. Products obtained with some of the early iron catalysts contained diolefines, and could not be satisfactorily refined by this means, but no difficulty has been experienced with the later iron catalyst products.

Ruhrchemie 'Hot' Clay Refining Process

Ruhrchemie found that the octane number of olefinic spirits can be raised by vapour-phase treatment at 250 - 350°C. in the presence of acid activated clays such as Granosil and Tonsil. The effect is considered to be due partly to movement of the double bond towards the centre of the chain and partly to isomerisation of the carbon chain. Purely paraffinic spirits do not respond to the process and

the rise in octane number increases with increase in the olefine content. No cracking takes place during the treatment and only a small amount of polymer is found.

In small scale trials the results given in Table 57 were obtained.

Table 57.

Hot Clay Refining. Ruhrchemie

Starting Material	Primary active carbon spirit	T.V.P. cracked spirit	Dubbs cracked spirit
d_{15}	0.692	0.720	0.719
Olefines, %	41	59	83
Octane number	40	60.5	61.5
Treated Material			
Octane number	54	70	81.5
Increase in octane number	14	9.5	20

Large scale tests were carried out using a tower containing 10 tons of activated clay and passing 3.6 cu.m./h. of vapourised spirit preheated to 400°C., the temperature in the tower being about 300°C. Spirit from the cracking of Diesel oil showed an octane number increase from 56 to 70, and the overall loss was 2%, 1% being due to polymer formation.

Based on these large-scale tests, the cost of the process, including capital and erection costs, was calculated as 0.6 Rpfg. per kg. of spirit treated.

Analysis of Reaction Products from Iron Catalyst Experiments.

The reaction products obtained when using iron catalysts contain, in addition to paraffins and olefines, alcohols and

various oxygen-containing substances distributed between the oily and aqueous portions of the product. The method of analysis used by Ruhrchemie in their pilot plant experiments was as follows:-

The portions of product recovered from the various collecting vessels were mixed and the aqueous layer separated. The latter, which contains alcohols but no hydrocarbons, is distilled until 10% has been collected. The distillate, which contains all the alcohols, separates into two layers, the upper layer consisting of higher alcohols and a lower aqueous layer containing lower alcohols, mainly ethyl, which are determined by conversion into the formic acid esters.

The hydrocarbon layer is distilled, cuts being made at 150°, 200°, 320° and 460°., vacuum being used for temperatures above 200°C. A small amount of water separates from the fraction boiling below 150°C. The density, refractive index, iodine number, hydroxyl number, acid number, saponification number, carbonyl number, and percentage removed by treatment with sulphuric-phosphoric acid mixture are then determined for each fraction.

Sulphuric acid-phosphoric acid mixture removes olefines and all oxygen-containing substances. It also attacks the more highly branched chain paraffins and the difference between the amount of material removed by this reagent and the amount of olefines and oxygen-containing substances in the original fraction gives an approximate indication of the extent of branching of the paraffins. Ruhrchemie do not consider that there is any reliable method for determining the proportion of iso-paraffins in mixtures of these with normal paraffins.

Analysis of Olefines

Dr. Büchner of Ruhrchemie determined the proportion of olefines in the primary and secondary products of the synthesis by ozonisation followed by treatment with moist silver oxide and determination of the formic acid produced. By this method he found that in the primary product obtained by synthesis with cobalt catalyst at normal pressure the percentage of the olefines with the double bond in the α-position was 8 - 12, whereas for medium pressure synthesis with water-gas recirculation it was 35, and in the material obtained by cracking normal cobalt catalyst product in a Dubbs unit it was 68.

Dr. Rottig, of Ruhrchemie, had worked out a method in which close fractions of the hydrocarbon mixture were oxidised by heating with nitric acid (d = 1.25 to 1.30) in the presence of V_2O_5 or AgO as activators.

The α-olefines give a fatty acid + CO_2 and are estimated by determining the latter with baryta. Other olefines give two molecules of fatty acids, and by analysis of the mixture of acids produced, the proportion of olefines with double-bonds in various positions can be estimated. It is claimed that the proportion of normal to branched chain olefines can also be determined by this method. Further details of the method are given in a document prepared by Dr. Rottig.