

(E) Methods of Manufacture of Catalysts for Hydrogenation and related processes.1. Molybdenum-Grude catalyst (for liquid phase hydrogenation of heavy oils).

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| Composition: | Grude | 98% |
| | MoO ₃ | 2% |

Grude containing 40-50% ash (obtained by carbonisation of brown coal in a Winkler generator) is treated with sulphuric acid to effect 90% neutralisation of its alkalinity. The neutralisation is made necessary by the fact that alkali poisons the molybdenum catalyst. The Grude is impregnated with an ammonia molybdate solution to give 2% MoO₃ in the finished catalyst. It is then dried at 140°C and ground to a fine powder (60% through 10,000 mesh). The catalyst is used as a 40% paste in asphalt-free oil.

2. Iron-Grude Catalyst (for liquid phase hydrogenation of heavy oils).

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| Composition: | Grude | 90% |
| | FeSO ₄ .7H ₂ O | 10% |

For this catalyst the Grude is not neutralised. The impregnation with hot concentrated iron solution is carried out in a screw conveyor. An amount of NaOH solution equivalent to the iron is then added. The catalyst is dried to an 18% water content and then pasted with oil.

3. 5058: Vapour Phase Saturation Catalyst (also used in T.T.H. process and formerly used in a combined saturation splitting process).

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| Composition: | WS ₂ | 100% |
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500 kg. H₂WO₄, alkali and chlorine free, is dissolved in 1200 litres mother liquor in an agitator. The mother liquor, from an earlier operation, contains 9 - 10% NH₃, 10 - 12% H₂S and 2 - 3% WO₃ as (NH₄)₂WS₄ in solution. Before adding the H₂WO₄, however, the NH₃ content of the mother liquor is brought up to 12 - 13% by addition of liquid ammonia. Solution requires ca 1½ hrs. at 150 mm Hg pressure and 60-70°C, and gives a solution containing the equivalent of 27% WO₃. 3 - 4% WO₃ remains undissolved and is filtered off as a sludge; the sludge contains some silica and is returned to the H₂WO₄ plant. The filtered solution is introduced at 50° C to either of two saturators where it is gassed with H₂S under 200 mm. Hg pressure while stirred. During the first half-hour the temperature is raised to 60°C and then maintained at 60°C for 3½-5 hrs. After a further 2 hrs. at 50°C the solution is cooled to 20° C over 2½ hrs, being stirred under H₂S all the time. Yellow crystals of (NH₄)₂WS₄ separate and the filtered solution shows only 4gWO₃/100 ccs.

The yellow crystals are filtered off under 0.5 atm. nitrogen pressure and after running off the filtrate a current of nitrogen at 60° C is drawn through the cake. The yellow salt is finally dried at 100-120°C in nitrogen in a rotating or stirred drier and then has the following composition: 9-10% NH₃, 54% W, 36.8 - 37.0% S.

The decomposition of the yellow salt to WS_2 is carried out in a scroll-type furnace which has two passes, each 8 m long. The first pass is electrically heated along the whole of its length, the second pass along only half its length, the second half of the second pass serving as an atmospheric cooler. The maximum temperature of the hot section of the furnace is maintained at 420-450°C and the residence time is ca 1 hr. A hydrogen rate of up to 100% in excess of the theoretical requirements is maintained through the furnace. The black powder has the following analysis: 73-74% W, 25-26% S, ca 0.1% H_2O , 0.1-0.2% H_2SO_4 .

The powder is milled in a hammer-type ("schlagkreuz") mill to the following grading:

70 - 80% through 10,000 mesh
100% " " 7,000 "

and is then pelleted. The last two operations also are carried out in an N_2 or CO_2 atmosphere and, after breaking off their edges in a rotary sieve, the pellets are stored under N_2 in gas-tight drums, since oxidation by air results in a loss of activity which cannot be restored.

The life of the catalyst depends on the nature of the middle oil but normally extends to two years. When used in the T.T.H. process, the life depends on the ash content of the charge. Although the activity can sometimes be restored by grinding and re-pelleting, it is eventually necessary to regenerate by roasting pellets to WO_3 in air and repeating the whole preparation via the yellow salt.

4. 6434 : Vapour Phase Splitting Catalyst (has occasionally been used direct on petroleum (120-325°C) and brown coal tar middle oils).

Composition: Terrana (Fuller's earth) 90%
 WS_2 10%

Not all Fuller's earths are catalytically active and it is necessary to test each particular sample for activity. 200 kg. earth, 200 l. of 10% HF and sufficient tungsten solution to give 10% WS_2 , in the finished catalyst are introduced into an Eirich mixer and the mixture kneaded for half an hour. The tungsten solution is prepared by dissolving yellow salt in mother liquor to give a solution containing 75 - 80 g. WO_3 /l. The slurry from the mixer is dried in an L.P. steam-heated stirred pan at 120°C. After cooling, the product is coarsely milled and then sulphided in the 5058 scroll-type furnace - temp. 425°C; residence time 1 hr, atmosphere H_2+H_2S . The sulphided powder is cooled in a nitrogen stream, kneaded with 30% of water in a small Eirich mixer and then pelleted damp. The pellets are first allowed to dry in the air for 3-4 hours and then dried at 120-130°C in an inert atmosphere. Finally, the pellets are heated in H_2 to 80°C for a day, to 120°C for 2 days, to 450°C for 12 hours and then cooled off in a stream of N_2 . Packaging and storage are on the same lines as for 5058.

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5. 3510 : Vapour Phase Aromatising Catalyst - now suspended by D.H.D. Process. (has been used as a saturation catalyst and as catalyst in the T.T.H. Process).

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| Composition: | MoO ₃ | 53.5% |
| | ZnO | 30% |
| | MgO | 16.5% |

21.6 kg. of MoO₃, 12.15 kg. of ZnO and 6.75 kg. of MgO are mixed dry in a mixer for 5 minutes; 15 - 17 l. of water are added and further mixed for about 20 minutes. The paste is spread on trays, allowed to stand for 2 - 4 hours, cut into pieces and further dried for about 12 hours at 120 - 140°C. After drying, the catalyst breaks up into separate pieces which, after sieving, are used as catalyst. The sieving is carried out on an 8 mm. mesh screen and gives 7 - 10% fines, which are added to the raw materials for the next batch.

If required in the pelleted form, dry cake is ground in a hammer mill. 8.8 kg. of the powder is mixed with 1.2 kg. of raw materials which have been previously mixed in the correct ratio and then 8 - 10% water added in an Eirich mixer. The moist material is then suitable for pelleting. As freshly prepared, the catalyst is not sensitive to oxygen.

6. 7846 : Vapour Phase Saturation Catalyst. (first substituted for 5058, later superseded by 8376).

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| Composition: | Al ₂ O ₃ | 87% |
| | MoO ₃ | 10% |
| | Ni ₂ O ₃ | 3% |

The carrier is an alumina that is prepared from technical alumina containing 60% Al₂O₃ and 40% water. This alumina is dissolved in NaOH, and reprecipitated with nitric acid, the acid additions being made as quickly as possible at a pH of 5.5 - 6.5 at a temperature not exceeding 50°C. The precipitate is filtered through a filter press and washed with water for a short time. After re-slurrying with water, the alumina is again filtered and washed with water until alkali-free. The filter cake is dried at 200°C and then powdered. After peptizing with about 2% HNO₃, the paste is spread on aluminum trays, partially dried, cut into cubes of 1 - 2 cm. sides, slowly dried and then calcined at 400 - 500°C. The cubes are washed with 5% ammonia solution and again ignited. They are then soaked with an ammoniacal molybdic acid solution, dried, soaked with a solution of nickel carbonate in acetic acid, and finally ignited at 500 - 600°C. If sulphuric acid is used in place of nitric acid, NiSO₄ is converted to NiS in the presence of H₂ at 400°C.

7. 8376 : Vapour Phase Saturation Catalyst (has also been used for the T.T.H. Process, for reduction of higher alcohols and for hydrogenation of di-isobutylene. Sometimes known as 7846_w 250).

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| Composition: | Al ₂ O ₃ | 70% |
| | WS ₂ | 27% |
| | NiS | 3% |

I.C. 7375

The alumina used as carrier is prepared from technical aluminium sulphate containing 18% Al_2O_3 . The raw $Al_2(SO_4)_3$ is dissolved in water at 50-70° C. to give a solution containing 10 - 12% Al_2O_3 and is then precipitated with a 20% ammonia solution. A slight excess of ammonia is used, the quantity being such that 20 cc of filtrate is equivalent to 10 cc of N/10 sulphuric acid. The precipitate is washed with a 0.1% ammonia solution until free from sulphate. The filter cake is dried to an ignition loss of 15 - 20%. After addition of 1% graphite, the mixture is pelleted and the pellets calcined at 450° C.

The pellets are saturated with an ammoniacal solution of WO_3 and $NiSO_4$, dried in an air stream at 140° C and then converted to the sulphide in an H_2S stream at 400 - 450° C. The pellets are then powdered, the powder repelleted and the pellets again treated with H_2S .

8. 5615: Vapour Phase Saturation Catalyst. (specially applicable to hydrogenation of di-isobutylene. Has also been used for reduction of higher alcohols and improvement of lubricating oil.)

Composition: WS_2 85%
 NiS 15%

100 parts by weight of H_2WO_4 is mixed dry with 24 parts of nickel carbonate in a ball mill for one hour and then pasted in a stirred vessel with 100 parts water. The paste is dried for about 6 hours and the dried mass pulverized. The powder is sulphidized to a 28 - 30% sulphur content in the scroll-type furnace used for 5058. The sulphidized powder is pelleted in the same way as 5058. An alternative method of manufacture, giving a catalyst referred to as 6718, involves the mixing of the corresponding amounts of ammonium sulpho-tungstate and nickel carbonate in a ball mill. The mixture is then converted into the sulphide at 450° C, and pelleted as described in the preparation of catalyst 5058.

9. 7360: D.H.D. Catalyst. (also referred to as 5436)

Composition: Al_2O_3 90%
 MoO_3 10-12%

An alumina carrier prepared from commercial alumina containing 60% Al_2O_3 and 40% water, is used. Cubes of alumina are prepared and ignited as described under Catalyst 7846. The cubes are soaked with an ammoniacal MoO_3 solution (20% NH_3) so that the finished catalyst contains 10-12% MoO_3 . After impregnation, they are dried at 140° C and ignited at 400° C to remove ammonia. The catalyst is then screened and packed.

10. 7935: Improved D.H.D. Catalyst. (gives slightly better yield than 7360, but requires shorter cycle times).

Composition: Al_2O_3 85%
 MoO_3 15%

The carrier is an alumina prepared from technical aluminium sulphate containing 18% Al_2O_3 . This raw material is brought into a concentrated

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solution at 50-70°C. and precipitated with 20% ammonia solution at 92-95°, filtered hot and washed. The filter cake is dried to a content of 80% Al_2O_3 , pelleted and the pellets calcined at 450°C. The pellets are then soaked with an ammoniacal MoO_3 solution, so that the final catalyst contains 15% MoO_3 . After impregnation, the pellets are dried at 140°C and calcined at 400° until the ammonia is removed.

11. 7019 : Aromatisation Catalyst.

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| Composition: | Activated charcoal | 80% |
| | Chromic Oxide | 15% |
| | Vanadium pentoxide | 5% |

Anthracite coal, peat and bituminous coal tar pitch are finely ground, mixed in the ratio of 100:10:40, dried with stirring 2 hours at 110°, ground and pelleted. The pellets are lightly sintered in a drying chamber at 100-120°C., then carbonised in a rotating kiln at 500°C, and finally activated in a vertical-pipe furnace with steam at 800-900°C. The activated pellets are soaked first with a saturated (6%) aqueous solution of ammonium vanadate, and then with a 40-50% aqueous solution of chromic acid, the pellets being dried after each impregnation. The amounts of the solutions are so controlled that the finished catalyst contains 15% Cr_2O_3 and 5% V_2O_5 . The catalyst has good mechanical strength and cannot be broken by hand.

12. Methane Steam Catalyst.

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| Composition: | Ni_2O_3 | 25% |
| | MgO | 14% |
| | Cement | 28% |
| | Kaolin | 33% |

Metallic nickel is dissolved in 40% Be nitric acid. The resulting solution, which is somewhat alkaline from the ammonia formed, is precipitated at 60°C with sodium carbonate and the filtered nickel carbonate is washed free from sodium nitrate. The nickel carbonate is mixed with sulphur-free MgO and kaolin and heated on aluminium trays in an electric oven at 400°C. It is then ground to 0.4 mm. size and mixed with sulphur-free alumina cement. After the addition of 15% water, the material is rapidly pelleted in a small Kilian press. The pellets are broken without delay into 1-2 mm. granules and the granules formed into Raschig rings in a Wilkinson press.

13. Water Gas Shift Catalyst - Brown Oxide.

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| Composition: | Fe_2O_3 | about 85% |
| | Cr_2O_3 | " 15% |

Details of preparation not obtained.

I.C. 7375

14. 6448 : Butane Dehydrogenation Catalyst.

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| Composition: | Al ₂ O ₃ | 90% |
| | K ₂ O | 2% |
| | Cr ₂ O ₃ | 8% |

22.5 kg. finely powdered activated alumina, 2 kg. water-soluble alumina, 1.5 kg. KOH, 1.6 kg. Cr₂O₃, and 2.7 l. 62% nitric acid are kneaded for about 40 minutes in a kneader lined with stainless steel. During the process, 7-9 l. of water are added. The plastic mass is extruded and then formed into spheres on a special stainless steel machine. The spheres are dried at 150°C for 16 hours and then ignited at 450°C until nitrate-free. K₂O has proved to be the most suitable alkali for inclusion in this catalyst.

15. Polymerisation Catalyst.

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| Composition: | SiO ₂ | 6.45% |
| | Al ₂ O ₃ | 0.30% |
| | Fe ₂ O ₃ | 0.28% |
| | CaO | 0.71% |
| | MgO | 11.09% |
| | SO ₃ | 0.1% |
| | Na ₂ O | 0.09% |
| Total | P ₂ O ₅ | 65.73% |
| Free | H ₃ PO ₄ | 26.75% |
| | H ₂ O | 1.23% |

46 kg. of phosphoric acid (1.698 gravity, 84%. Analysis 62.44% P₂O₅ / 2% H₃PO₂) is poured into a 150 l. steel (V4A) pot, and a suspension of 5.55 kg. magnesia* in 10 l. H₂O is slowly added to the phosphoric acid. This is followed by rapid addition at 80°C of 3.32 kg. of kieselgu (13% volatile matter content) suspended in 13 l. H₂O. To this is further added 9 kg. of catalyst powder from a previous preparation which is wetted with 9 l. H₂O. The total water content is 36 l., 4 l. having been used to wash out the charging vessels. The mass is

* Obtained from "Zillertaler Magnesitwerke", the magnesia had the following composition:

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| CaO | 2.7% |
| Al ₂ O ₃ / Fe ₂ O ₃ | 1% |
| K ₂ O | 0.15% |
| Na ₂ O | traces |
| Cl | 0.036% |
| SO ₄ | 1.9% |
| MgO | 87.6% |
| H ₂ O | 6.21% |
| SO ₂ | 0.7% |

stirred and kept at 84-112°C for 22-27 hours. The viscous mass is then poured on aluminium trays and dried at 120°C under a low vacuum (40-70 mm.). The catalyst is then cut into cubes and dried for an additional 46 hours at about 120°C. The total weight of the recovered material is about 52 kg. The cubes have a crushing strength of 7-13 kg/cm² and an apparent density of 0.8.

16. 6752 : Catalytic Cracking Catalyst.

Composition: Al₂O₃ 33%
 SiO₂ 67%

Commercial waterglass solution (26% SiO₂) is treated with an excess of concentrated (76%) hydrochloric acid to form a sol without gel precipitation. To this SiO₂-sol aluminium nitrate solution is added in proportion to the desired final composition of catalyst. The acidic SiO₂-Al₂O₃ solution is precipitated at 90°C and a pH of 5.5-6.0 (antimony electrode) by continuously adding small amounts of ammonia solution. The precipitate is filtered and washed with hot water until free from alkali and chloride. The filter cake is then dried at 110°C, powdered, pelleted, and activated in the presence of air by heating at 450° (2 hours to 450°, 6 hours at 450°).

This catalyst is less sensitive to steam and temperature than are catalysts based on Fuller's earth.

The catalyst can be used at temperatures up to 650°C; but loses all activity on heating to 800°C. Catalyst based on Fuller's earth can be used only up to 550°C.

VI. LUBRICATING OIL

There was no commercial production of synthetic lubricating oil at Ludwigshafen, but 30-50 tons/day of crude oil was brought in from Brücksel, near Karlsruhe, and was subjected to conventional refining to products including lube oils. The plant capacity is 500 barrels of crude oil per day. A flow diagram of the plant is attached as Fig. XVIII.

The crude oil is distilled in a two column atmospheric-vacuum tube still provided with two side stream draw-offs on the atmospheric tower and three draw-offs on the vacuum tower.

Straight-run gasoline is taken overhead on the atmospheric tower, treated with sulphuric acid, neutralized with caustic soda and water-washed. Kerosene is taken off the upper draw-off on the atmospheric tower, treated with sulphuric acid, neutralized and water-washed. Light gas oil is taken off the lower draw-off on the atmospheric tower. The reduced crude from the bottom of the atmospheric tower passes through a second fired heater to the vacuum tower.