

FORM 1
COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

I\We,

UNILEVER PLC

of

UNILEVER HOUSE
BLACKFRIARS
LONDON EC4
ENGLAND

618953

hereby apply for the grant of a standard patent for an
invention entitled:

HYDROGENATION CATALYST

which is described in the accompanying complete specification

Details of basic application(s):

Number of basic application	Name of Convention country in which basic application was filed	Date of basic application
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87 200855.2

EP designating GB et al.

08 MAY 87

My/our address for service is care of CLEMENT HACK & CO., Patent
Attorneys, 601 St. Kilda Road, Melbourne 3004, Victoria,
Australia.

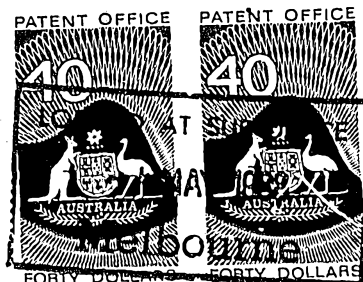
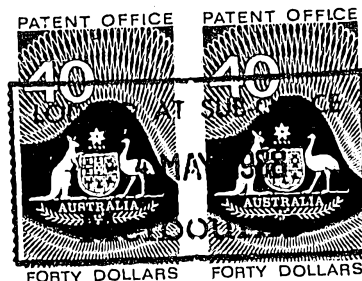
DATED this 04th day of May 1988

UNILEVER PLC

CLEMENT HACK & CO.

[Handwritten signature]

TO: The Commissioner of Patents.



[Handwritten '160' and 'NO' over a stamp]

LODGED AT SUB-OFFICE

- 4 MAY 1988

Melbourne



CLEMENT HACK & CO

Australia Patent Declaration Form

Forms 7 and 8

AUSTRALIAPatents Act 1952DECLARATION IN SUPPORT OF A CONVENTION OR NON-CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITION

Name of Applicant(s) In support of the application made by UNILEVER PLC

Title HYDROGENATION CATALYST

Name and address of person making declaration: I, Dilshad Rajan,
Authorized Signatory
of Unilever House, Blackfriars, London E.C.4, Great Britain,

do solemnly and sincerely declare as follows:-

1. I am authorized by the abovementioned applicant to make this declaration on its behalf.
2. The basic application as defined by Section 141 of the Act was made in the following country on the following date by the following applicant(s) namely:-

Country, filing date and name of Applicant(s) for the basic application: in EUROPE on 8th May 1987
by UNILEVER N.V. designating GB and other Convention countries.

3. The said basic application was the first application made in a Convention country in respect of the invention/the subject of the application.

Name(s) and address(es) of the or each actual inventor 4. The actual inventors of the said invention are: VAN BEEK, Wilhelmus Petrus, Thomas à Kempisstr.144, 3132 CK Vlaardingen, Holland; DEN HOED, Ms Wilma, Frans Halsstr. 65, 3351 VD Papendrecht, Holland; VAN LEEUWEN, Willem Aart, Johan Willem Frisolaan 54, 3136 BK Vlaardingen, Holland; POELS, Eduard Karel, Oude Rijn 128, 2312 HK Leyden, Holland; and VISSER, Cornelis, Plutostraat 24, 3331 SL Zwijndrecht, Holland.

See reverse side of this form for guidance in completing this part 5. The facts upon which the applicant is entitled to make this application are as follows:-
The said applicant UNILEVER PLC is the assignee of the said basic applicant UNILEVER N.V., and the said UNILEVER N.V. was the assignee of the said actual inventors Van Beek, Den Hoed, Van Leeuwen, Poels and Visser.

DECLARED at London this 28th day of April, 1988



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- (56) Prior Art Documents
US 4495307
US 4490480
US 4081353
- (57) Claim

1. A nickel upon transition alumina catalyst containing 5-40% ww of nickel, with an active nickel surface area between 80 and 300 m²/g of Ni, characterised in that the transition alumina satisfies the following X-ray diffraction pattern:

d (10 ⁻¹⁰ m)	I/I ₀
1.39	100
2.85	75-85
2.72	60-80
2.43	70
2.01	45-80

2. A catalyst according to claim 1, characterized in that the BET-total surface area of the catalyst is between 50 and 200 m²/g catalyst.

3. A catalyst according to claim 1 or 2, characterized in that the transition alumina is substantially free from pores with a radius below 2.0 nm.

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(10) 618953

4. A catalyst according to any one of claims 1, 2 or 3, characterized in that the catalyst has a pore size distribution substantially between 3.5 and 30 nm.

8. A process for hydrotreating unsaturated hydrocarbons, characterized in that unsaturated hydrocarbons are treated with hydrogen in the presence of a catalyst as claimed in any one of claims 1 to 7.

9. A process according to claim 8, characterized in that petroleum distillates are treated, and aromatic hydrocarbons therein are at least partly hydrogenated.

AUSTRALIA
PATENTS ACT 1952

Form 10

COMPLETE SPECIFICATION

(ORIGINAL)
FOR OFFICE USE

618953

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TO BE COMPLETED BY APPLICANT

Name of Applicant:

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Australia.

Complete Specification for the invention entitled:
HYDROGENATION CATALYST

The following statement is a full description of this invention
including the best method of performing it known to me:-

1^AHYDROGENATION CATALYST

The invention relates to a nickel upon transition alumina catalyst, and more in particular to such a catalyst with a nickel content of 5-40% ww and an active nickel surface area between 80 and 300 m²/g of nickel.

Many catalysts are of the type of a metal which has been dispersed as the active phase on a carrier or support material and, confining ourselves to petroleum chemistry, many carrier materials have been proposed. In the Oil and Gas Journal of October 5 (1987), pages 41-78, the following supports have been named: alumina, gamma-alumina, alpha-alumina, zinc aluminate, calcium aluminate, magnesium aluminate, alumina-molybdenum oxide, amorphous and crystalline silica-aluminas, molecular sieves/zeolites, zeolite-aluminas, kieselguhr/diatomaceous earth, activated carbon, polystyrene-divinylbenzene copolymers, pumice and sepiolite.

More specifically, nickel upon transition alumina and, more in particular, gamma-alumina are known from US-A-4 490 480 (Octropa B.V.). These catalysts, however, have a relatively small pore radius and not a very high active nickel surface area. Consequently, with substrate material of a high molecular weight transport (intra-particle diffusion limitation) problems occur so that the active nickel area is not completely available for hydrogenation reaction.

US-A-4 081 353 (Kehl et al.) discloses a process for the hydrodesulphurisation of a sulphur-containing charge-stock, using a catalyst comprising 2-25 weight

percent of a metalliferous hydrogenation component on an alumina hydrate with x-ray diffraction peaks at $2\theta = 14^\circ$ and, judging from the figures in this patent, $2\theta =$ about 28° and 38° . This pattern is typical for AlOOH , i.e. boehmite (ZCPPS file 21-1307). The peak at $2\theta = 14^\circ$ is the most intense peak in the x-ray diffractogramme of the boehmite; this peak is not found in the x-ray diffractogramme of θ -alumina.

- 10 GB-A-1 528 413 (Batty et al.) discloses a process for the production of white oils of DAB 7 quality (DAB = Deutsche Pharmakopoeia, 7th Ed.). Especially the second stage hydrogenation process described is interesting. In this process, applying a nickel-containing catalyst
- 15 supported on sepiolite is used. Sepiolite is a naturally occurring mineral (which can also be prepared via a synthetic route), mainly consisting of magnesium silicate.
- 20 US-A-4 495 307 (Clements et al.) discloses catalytic particles shaped as a cylinder of polylobate cross-section having bluntly rounded, concave, interlobar interstices. The aim of such forms is to extend the particle surface to volume ratios beyond those
- 25 encountered in simple cylindrical or spherical forms. Thus, the liquid hold-up in trickle flow operation processes is increased, also extending the residence time for the reactions improving the effectiveness of the catalyst. Oxides mentioned are alumina, silica and
- 30 silica-alumina with one or more active, metallic components selected from Group VI and Group VII of the Periodic Table of the Elements. The catalysts mentioned in the examples of this citation mostly possess a BET surface area above $150 \text{ m}^2/\text{g}$. It is
- 35 therefore necessary to investigate the catalyst preparation method referred to, viz US-A-3 232 887 (Pessemisis et al. In this document the preparation

is described of a number of catalysts containing at least one metallic element from Group VI of the Periodic Table and at least one element from Group VIII of the periodic table and at least a stabilizing amount of water-soluble orthophosphoric acid. Several supports are claimed, including alumina. In the examples of US-A-3 232 887, catalysts A through I are described, all prepared with alumina as a support. The BET surface areas of these catalysts are all above 200 m²/g.

Moreover, as the values of 950°F and 1250°F are described as calcination temperatures, it is obvious that calcining at these temperatures results in a support consisting substantially of gamma-alumina with some traces of delta-alumina.

US-A-4 471 144 (Arena) discloses theta-alumina as a hydrothermally stable support in hydrogenation processes, more in particular a method for hydrogenating a carbohydrate in aqueous solution to its polyols, using a catalyst consisting essentially of zero-valent ruthenium dispersed on theta-alumina. Apart from the fact that ruthenium is disclosed, the hydrothermal stability of the theta-alumina is highlighted since the process takes place in aqueous solution and this capacity of the theta-alumina is consequently essential for the process described.

The present invention provides novel catalysts containing 5-40% ww of nickel, an active nickel surface area between 80 and 300, preferably 100 m²/g of nickel and wherein the transition alumina satisfies the following X-ray diffraction pattern:

	d (10^{-10}m)	I/I ₀
	1.39	100
	2.85	75-85
	2.72	60-80
5	2.43	70
	2.01	45-80

This diffraction pattern is considered typical for theta-alumina. Preferably the BET-total surface area of the novel catalyst is between 50 and 200 m²/g catalyst.

In order to make sure that the nickel is readily available for hydrogenation reactions, the transition alumina is preferably substantially free from pores with a radius below 2.0 nm.

The contribution of pores with a radius below 2 nm to the total pore volume is virtually zero. More preferably the catalyst has a pore size distribution substantially between 3.5 and 30 nm, rather between 4.0 and 20 nm.

The catalyst may contain one or more promoters selected from the group consisting of Mo, V, Ce, La, Ba, Ca, Zn or Mg in an amount of 0.2-2.0 mole percent.

It has now been found that catalysts having an excellent selectivity and activity can be prepared by impregnating shaped theta-alumina particles with an ammoniacal metallic solution having a particularly high pH value, namely between 9 and 11, and subsequently evaporating the impregnated alumina particles to dryness, calcining and reducing.

The impression exists that better properties are connected with a very fine dispersion of the active phase and a decreased formation of a metal of Group

VIII, in particular nickel, aluminate, which metal aluminates are catalytically inactive.

During the evaporation of the impregnated carrier material to dryness, ammonia gas escapes, as a result of which the pH of the liquid drops.

If, in the ammoniacal metal solution, considerable amounts of anions of stronger acids occur, particularly of strong mineral acids, such as sulphuric acid and nitric acid, it can then be expected that these will bring about an important reduction of the pH, not only during the evaporation but already in the starting pH. It is therefore recommendable that the impregnation liquid (in the present case the ammoniacal metal solution) be completely or substantially free of anions which are derived from acids stronger than carbonic acid and particularly be free, or substantially free, of anions of strong mineral acids and free of anions strongly binding to transition metals such as anions of organic acids.

The ammoniacal metal solution can be prepared by dissolving Group VIII metal, more in particular nickel carbonate, in concentrated ammonia whilst refluxing and subsequent addition of ammonium carbonate and/or carbamate.

The present invention provides a novel, highly active catalyst with a well dispersed active phase. These catalysts are very active for application in hydrogenolytic processes, even when the catalysts contain low percentages of metal(s).

In practical situations the catalyst is applied in fixed bed, therefore the carrier material is best in the form of shaped particles, especially material, in which the cross-section of the carrier particles has a

polylobal shape, having concave or convex surfaces, more in particular trilobal and quadrulobal material is preferred.

- 5 In another embodiment of the invention a process is provided for hydrotreating unsaturated hydrocarbons, in which unsaturated hydrocarbons are treated with hydrogen in the presence of a catalyst as described above more in particular the invention provides a
10 process which a petroleum destillates are treated and aromatic hydrocarbons therein are at least partly hydrogenated.

- Hydrogenation processes according to the present
15 invention are particularly useful for the preparation of white oils in which a high boiling (b.p. 200-600°C) hydrocarbon is in a first step hydrotreated with a supported nickel/molybdenum or supported cobalt/molybdenum catalyst (as according to DE-A-
20 3 221 076 (BASF) in the first step) and subsequently hydrotreated (hydrogenolysis) with a catalyst according to the present invention. White oils are colourless and odourless low-aromatic or aromatic free mineral oil products boiling in the range of heavy gas oils, vacuum
25 gas oils and residual oils. With respect to different quality requirements, they find application in the plastics, food, cosmetics and pharmaceutical industries.

- 30 Hydrogenation processes according to the present invention are also very useful for solvent hydrogenation in which a refined petroleum fraction with a boiling range between 100° and 250°C is hydrotreated with a catalyst as defined above.
35 Applications of such solvents include: as diluent for inks, paints, insecticides, cleansing product manufacture, as an extracting solvent in chemical, pharmaceutical, cosmetics and food industries.

The invention is illustrated by the following examples:

Examples 1-4

5 A commercially available gamma- Al_2O_3 extrudate (trilobe; 1.3 mm diameter; 265 m^2/g BET surface area) was calcined for 2 hours at 1050°C, yielding predominantly theta- Al_2O_3 as evidenced by X-ray diffraction; the BET surface area was reduced to ca.
10 100 m^2/g . The pore volume of these theta- Al_2O_3 extrudates was impregnated by submersion in a nickel-containing solution (approximately twice the total pore volume was used) for 5 to 10 minutes. The impregnating solution was prepared in the following way:

15 In 1 litre of 25% NH_4OH solution in water, 176 g of ammonium carbamate ($\text{NH}_4\text{CO}_2\text{NH}_2$) and subsequently 235 g of nickel hydroxycarbonate (46-49% Ni) were added slowly. The mixture was heated very carefully to
20 approximately 50°C and refluxed for 3 hours at this maximum temperature or slightly below. The resulting nickel complex solution contains $(\text{NH}_3)_6\text{NiCO}_3$ at a concentration of 0.112 g Ni/ml or 0.142 g NiO/ml. The solution was applied as such as described above or used
25 after filtration, centrifuging or decanting to remove traces of precipitates yielding ca. 0.135 g NiO/ml.

After impregnation of the extrudates, these are filtered and the filtrate collected for re-use. Drying
30 was performed at ca. 120°C for several hours. The dry catalyst is calcined at 300-350°C.

The calcination step caused a better recovery of pore volume than drying alone, and resulted in higher nickel
35 content of the catalyst after subsequent impregnation steps. Typically, nickel contents of 11-17% nickel were obtained after three impregnation steps (see Table I). Nickel contents were determined by X-ray fluorescence

spectroscopy; internal surface area, pore volume and pore radii by nitrogen physisorption, nickel surface area by H_2 -chemisorption and degree of reduction of the reduced catalyst determined by measuring H_2 evolution after submersion in 5N H_2SO_4 at increased temperatures.

The catalysts were reduced in H_2 at 500°C maximum temperature and passivated in nitrogen flow containing 0.05% O_2 at ambient to 80°C temperature, increasing the O_2 content slowly to 20%.

Table I

Example	Ni (wt.%)	DR (%)	S_{Ni} (m^2/g Ni tot)	CS nm	RP nm	BET m^2/g cat.
1	12.6	83	174	2.1	10.1	80
2	14.2	75	184	1.8	7.4	99
3	13.0	85	198	1.9	7.5	110
4	16.2	88	164	2.3	10.3	77

DR = Degree of Reduction as determined by measuring the H_2 evolution from the reaction of the Ni^0 present in the weighed sample with 5N H_2SO_4 using a burette to which the same glass vessels used for chemisorption measurements were connected.

CS = Crystallite Size (= diameter), calculated from active nickel surface area.

RP = Average Pore Radius as calculated from nitrogen physisorption measurements.

S_{Ni} = Active nickel surface area as determined by hydrogen chemisorption at 760 m.bar.

(General methodology, R.Z.C. van Meerten et al., Surface Science 135 (1983) 565 ff).

Application testing

1. A feedstock characterized by the following parameters: boiling range 157-193°C; density 0.78 (15°C); 21% aromatics; sulphur content 1 mg/kg, was hydrogenated using a catalyst prepared according to Example 1 under the following conditions:

Pressure : 40 bar
 H₂/oil : 175 ml/ml
 temperature : 75-180°C
 LHSV : 4 h⁻¹
 catalyst volume : 9 ml

The results are summarized in Figure 1. As a reference, a standard co-precipitated and extruded 55% Ni/Al₂O₃ catalyst was used; at 150°C, e.g. the relative activity of the catalyst prepared according to this example with respect to the reference was 395% (at 125°C : 180%).

$$\text{RWA}^* = \frac{(C_A \text{ sample})^{1-n} - (C_A)^{1-n}}{(C_A \text{ ref})^{1-n} - (C_A)^{1-n}} \times 100\% \quad (n = 1.3)$$

2. A technical white oil feedstock containing 2.7% aromatics and 75 ppm sulphur; flashpoint 227°C; viscosity 272.0 m²/s and a UV absorption at 275 nm of 83 was treated over a catalyst prepared according to Example 2 at an LHSV of 1.5 h⁻¹; H₂/oil = 175 Nm³/m³; 95, 70 and 40 bar pressure, at 200°C, 175°C and 150°C at each pressure; catalyst volume 9 ml (crushed particles with 6 g SiC diluent).

As a reference, a catalyst prepared according to DE-A- 3 221076 (BASF) was used. The results are summarized in Figure 2. At 95 bar pressure and 150°C the relative activity of the claimed catalyst with respect to the reference was 260% (at 175°C: 160%).

(calculated as follows:

$$RWA^* = \frac{(C_A \text{ sample})^{1-n} - (C_A)^{1-n}}{(C_A \text{ ref})^{1-n} - (C_A)^{1-n}} \times 100\% \quad (n = 1.3)$$

5

* RWA = Relative Weight Activity

Example 5

- 10 A technical white oil (C-oil) characterized by a UV-absorption value at 275 nm of 105; containing 7 ppm sulphur and 2.7% aromatics; having a density (at 15°C) of 885 kg/m³; a viscosity of 325 m²/g at 20°C; and a flash point of 236°C, was hydrogenated, applying a catalyst prepared according to Example 3. The catalyst bed volume was 79 ml diluted with 265 g of silicon carbide particles with a diameter of 1 mm. The liquid hourly space velocity was 0.15 h⁻¹; H/oil ratio 1000 Nm³/m³; the pressure 200 bar; and the temperature
- 15 220°C.
- 20

The odourless, colourless, substantially sulphur-free product obtained after several days equilibration was characterized by Table II. This table indicates no viscosity loss in the product and also that the product both passed the Hot Acid Carbonisable Substances test and is within the limits for UV-absorption (indicated in the table) according to DAB 8 (German Pharmacopoeia 8th edition).

25

Table II

	Density at 15°C (kg/m ³)	: 883
	Viscosity at 20°C (m ² /g)	: 323
5	Acid test DAB 8	: pass
	U.V.-A.:	
	275 nm (limit 1.6)	: 1.24
	295 nm (limit 0.2)	: 0.07
	300 nm (limit 0.15)	: 0.05

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A nickel upon transition alumina catalyst containing 5-40% ww of nickel, with an active nickel surface area between 80 and 300 m²/g of Ni, characterised
5 in that the transition alumina satisfies the following X-ray diffraction pattern:

	d (10 ⁻¹⁰ m)	I/I ₀
	1.39	100
	2.85	75-85
10	2.72	60-80
	2.43	70
	2.01	45-80

2. A catalyst according to claim 1, characterized in that the BET-total surface area of the catalyst is between
15 50 and 200 m²/g catalyst.

3. A catalyst according to claim 1 or 2, characterized in that the transition alumina is substantially free from pores with a radius below 2.0 nm.

4. A catalyst according to any one of claims 1, 2 or
20 3, characterized in that the catalyst has a pore size distribution substantially between 3.5 and 30 nm.

5. A catalyst according to any one of claims 1, 2 or 3, characterized in that the catalyst has a pore size distribution substantially between 4.0 and 20 nm.

- 25 6. A catalyst according to any one of claims 1 to 5, characterized in that the carrier material is in the form of shaped particles.

7. A catalyst according to claim 6, in which the cross-section of the carrier particles has a polylobal shape.



8. A process for hydrotreating unsaturated hydrocarbons, characterized in that unsaturated hydrocarbons are treated with hydrogen in the presence of a catalyst as claimed in any one of claims 1 to 7.

5 9. A process according to claim 8, characterized in that petroleum distillates are treated, and aromatic hydrocarbons therein are at least partly hydrogenated.

10 10. A process according to claim 8, characterized in that a high boiling (b.p. 200-600°C) hydrocarbon in a first step is hydrotreated with a supported nickel/molybdenum or supported cobalt/molybdenum catalyst and subsequently hydrotreated with a catalyst according to any one of claims 1 to 7.

15 11. A process according to claim 8, characterized in that a refined petroleum fraction with a boiling range between 100° and 250°C is hydrotreated with a catalyst according to any one of claims 1 to 7.

DATED THIS 23RD DAY OF OCTOBER 1991

UNILEVER PLC

20 By its Patent Attorneys:

GRIFFITH HACK & CO

Fellows Institute of Patent
Attorneys of Australia.



FIG.1

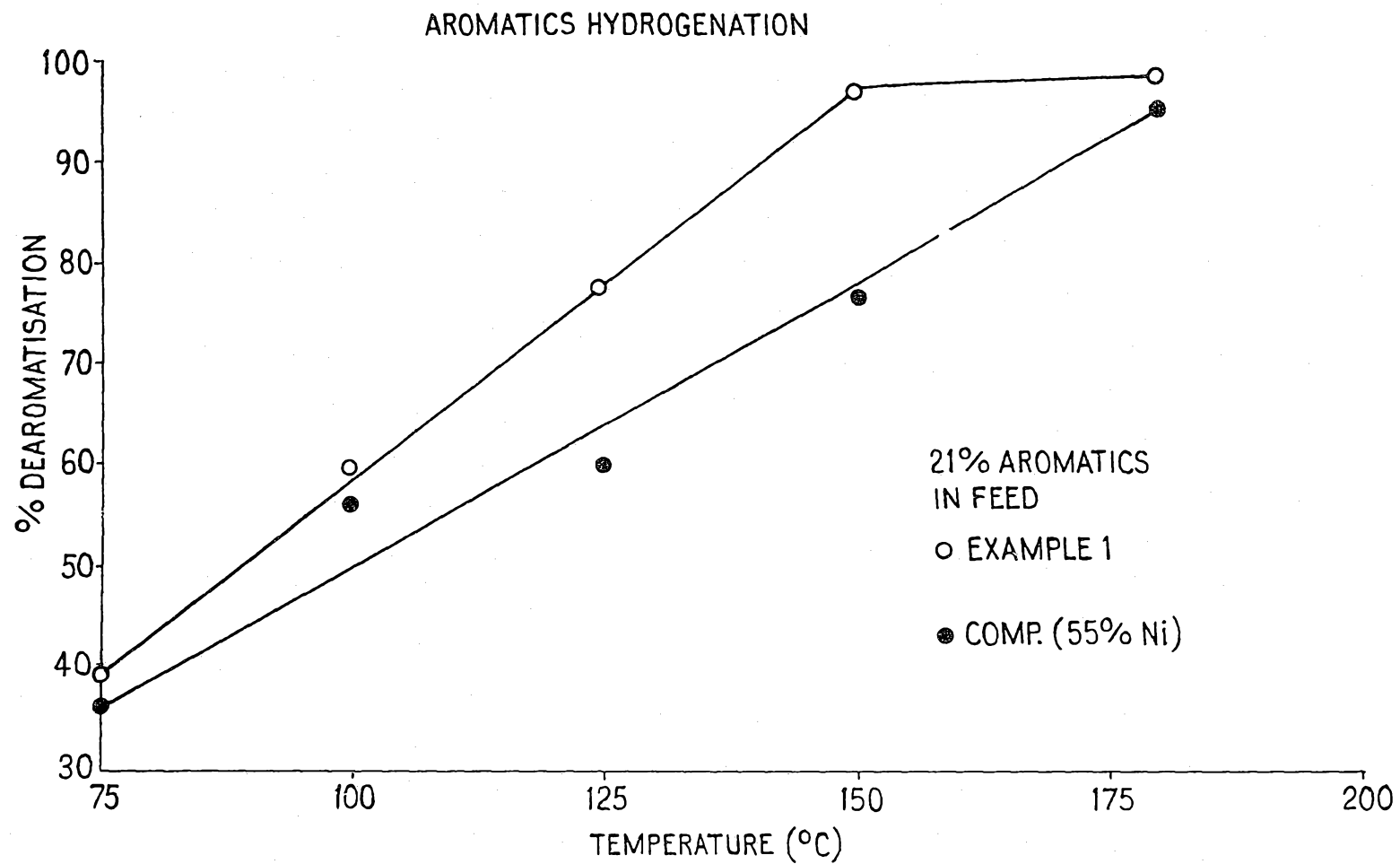


FIG.2

