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COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

Degussa Aktiengesellschaft, incorporated in the Federal Republic of Germany,
of Weissfrauenstrasse 9, D-6000 Frankfurt am Main, FEDERAL REPUBLIC OF
GERMANY, hereby apply for the grant of a standard patent for an invention
entitled:

A Catalyst for the Catalytic Gas-phase Oxidation of Olefins
to Unsaturated Aldehydes

which is described in the accompanying complete specification.

Details of basic application(s):-

Basic Applic. No: Country: Application Date:

P 39 30 533.3 DE 13 September 1989

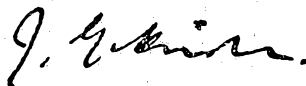
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DATED this TWELFTH day of SEPTEMBER 1990

Degussa Aktiengesellschaft

By:



Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 141173
S&F CODE: 53300

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT

In support of the convention application made for a patent for an invention entitled:

A Catalyst for the Catalytic Gas-phase Oxidation of Olefins
to Unsaturated Aldehydes

I/We, Dr. Wolfgang Merk
[full name of declarant(s)]

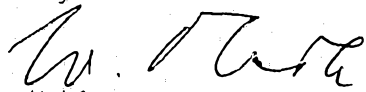
of ... Bergstrasse 44, D-6477 Limeshain 3, ...
[full address of declarant(s) - not post office box]

... Federal Republic of Germany
.....

do solemnly and sincerely declare as follows:

1. I am/~~We~~ are authorised by Degussa Aktiengesellschaft, the applicant for the patent to make this declaration on its behalf.
2. The basic application as defined by Section 141 of the Act was made in the Federal Republic of Germany on 13 September 1989 by Degussa Aktiengesellschaft.
3. Wolfgang Bock, of Am Hauser Graben 2, D-6456 Langenselbold; Dietrich Arntz, of Lorsbachstrasse 32, D-6370 Oberursel; Werner Burkhardt, of Reichenbachstrasse 9, D-6486 Brachtal 2, all in the Federal Republic of Germany and Gunter Prescher, of 10 Sherwood Drive, Larchmont, New York, 10538-2626 United States of America, respectively, are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:- Degussa Aktiengesellschaft is entitled by Contract of Employment between the inventors as employees and Degussa Aktiengesellschaft as employer as a person who would be entitled to have the patent assigned to it if a patent were granted upon an application made by the inventors.
4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention(~~s~~) the subject of the application.

DECLARED at Frankfurt/Main this 1st day of October 1990


... Dr. Wolfgang Merk
Signature of Declarant(s)

TO: THE COMMISSIONER OF PATENTS,
AUSTRALIA
SHEPHERD

(12) PATENT ABRIDGMENT (11) Document No. AU-B-62459/90
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 624024

(54) Title
A CATALYST FOR THE CATALYTIC GAS-PHASE OXIDATION OF OLEFINS TO UNSATURATED ALDEHYDES

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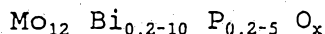
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(56) Prior Art Documents
US 4511671
EP 102641
EP 355664

(57) Claim

1. A catalyst for the production of unsaturated aldehydes from olefins, more particularly acrolein from propene, by oxidation with a gas containing molecular oxygen, characterized by the following properties in combination:

a) an active mass containing at least the elements molybdenum, bismuth, phosphorus and oxygen in atomic ratios of



and silicon-containing support material;

b) a catalyst element of any geometric shape in which the ratio of outer surface Q_p to volume V_p is above 1.6 mm^{-1} and of which the spatial dimension, defined by the diameter of a sphere which still just surrounds it, is smaller than 7.5 mm;

c) a porosity of the catalyst of at least 0.46, the absence of micropores ($< 2 \text{ nm}$), a mesopore volume (2 - 30 nm) of at least $0.03 \text{ cm}^3/\text{g}$ and

a macropore volume ($> 30 \text{ nm}$) of at least $0.30 \text{ cm}^3/\text{g}$;

d) a mercury density of the catalyst element of at least

1.25 g/cm³;

- e) a specific BET surface of at least 10 m²/g;
- f) a breaking strength of at least 6.0 N;
- g) an abrasion of less 50 mg/g catalyst;
- h) a pressure loss of less than 1,600 Pa/m of a catalyst bed introduced into a 2 cm diameter tube.

5. A process for the production of the catalyst claimed in any one of claims 1 to 4, characterized in that

- a) a suspension of the co-precipitate obtained in known manner by combining salt solutions of the catalytically active elements (except Si) is mixed with the insoluble silicon-containing solid and the suspension obtained is spray-dried under conditions which provide for an initial temperature of the drying air of 300°C to 600°C, a temperature during deposition of the dried powder of 120°C to 220°C and a spraying intensity designed to produce a spray-dried powder having an average particle diameter of less than 30 μm, the residence time of the spray-dried powder in the dryer being from 2 to 25 seconds,
- b) the spray-dried powder is calcined in a furnace, preferably a rotary kiln, over residence times of 5 to 60 minutes and at a peak temperature in the spray-dried powder of 320 to 480°C,
- c) the calcined spray-dried powder is extruded with 5 to 40% by weight, based on the quantity of spray-dried powder, of a pore-forming agent which decomposes completely at a temperature below 400°C and with wetting agents, lubricants and binders in a quantity sufficient to produce an extrudable mass, the wetting agents, lubricants and binders together making up no more than 40% by weight of the quantity of spray-dried powder, in the required geometric shape at a temperature below 80°C and under a pressure below 50 bar and the extruded strand is divided up by cutting to the length of the desired element,
- d) the extruded individual elements are dried, the decomposable substance present is carefully removed by

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(10) 624024

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burning out in a furnace, preferably a rotary kiln, and the individual elements are conditioned in an air stream for 5 to 60 minutes at a peak temperature, as measured in the bed of individual elements, of 450 to 650°C.

10. A catalyst for the production of unsaturated aldehydes from olefins substantially as hereinbefore described with reference to any one of the Examples.

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S & F Ref: 141173

FORM 10

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PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

Name and Address
of Applicant:

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Complete Specification for the invention entitled:

A Catalyst for the Catalytic Gas-phase Oxidation of Olefins
to Unsaturated Aldehydes

The following statement is a full description of this invention, including the
best method of performing it known to me/us

§ 017218 2000

5845/3

A b s t r a c t**A catalyst for the catalytic gas-phase oxidation of olefins
to unsaturated aldehydes**

The invention relates to a catalyst for the production of unsaturated aldehydes by oxidation with a gas containing molecular oxygen, in which an active mass containing at least the elements Mo, Bi, P and O and Si-containing support material is used in the form of a catalyst element having a certain ratio of outer surface to volume and a defined spatial dimension, porosity, density, specific surface, breaking strength, abrasion and gas throughflow capacity. The catalyst can be obtained by a special process to which the invention also relates.

A catalyst for the catalytic gas-phase oxidation of
olefins to a unsaturated aldehydes

Description

This invention relates to a catalyst for the heterogeneously catalyzed gas-phase oxidation of propene to acrolein which is used in tube bundle reactors.

5 The highly exothermic reaction of propene on heterogeneous catalysts with an oxygen-containing gas leads to a number of unwanted secondary products in addition to the desired product acrolein. It is known that local overheating of the catalyst and the resulting increased formation of secondary products can be avoided by effective dissipation of the heat of reaction, for example in tube bundle reactors.

10 It is also known that the pressure loss of a catalyst bed can be influenced by the size and external shape of the catalyst elements. The internal structure of the catalyst elements (porosity, length of the diffusion paths) critically determines mass transfer and heat transfer in the catalyst and, accordingly, has a major bearing on selectivity along with the composition of the catalytically active mass. High compressive strength and abrasion resistance are requirements which a catalyst has to satisfy for use on an industrial scale. High abrasion would mean that, during filling of the tubes of a tube bundle reactor, the scattering of the pressure losses of the individual tubes would be high, resulting in different throughflow rates and impaired selectivity.

15 20 25 DE-PS 31 25 061 describes a process for the production of acrolein using shell catalysts.

With shell catalysts, local overheating is avoided by the temperature-equalizing effect of the inert support; in the relatively thin shell, the diffusion paths for the

30

gaseous reactants are short.

DE-OS 33 38 380 describes catalysts for the oxidation of propene to acrolein which are made in the form of rings or hollow cylinders from a mass containing Mo, Fe, Bi and W. These catalysts may be assumed to have been derived from shell catalysts by replacement of the inert core of the shell catalysts by an "inert void", the shell being open on two opposite sides to allow the reactants access to the void. Compared with shell catalysts, these ring or hollow cylinder catalysts have a larger ratio of outer surface to volume. The active mass is thus more accessible to the reactants. The low pressure loss and high heat dissipation of the shell catalysts are again present. To ensure that the "hollow catalysts" have sufficient mechanical strength, the active mass is highly compressed, with the result that the inner structure is adversely affected.

EP-OS 0 184 790 describes ring-shaped catalysts, albeit with rounded end faces to improve fillability, but does not mention either the catalyst mass or a special production process; in particular, there is no reference to measures for producing a special, favorable inner structure.

In order to enable the active mass to be optimally utilized, the inner structure of the catalyst has to be such that a potentially high reaction velocity is not limited by obstacles to mass transfer within the catalyst.

An attempt along these lines is described in EP-OS 0 279 374 which relates to a process for the production of a catalyst containing Mo, Fe, Bi which is characterized by its specific surface, pore volume and pore distribution. On account of the production process, however, it is only possible to obtain catalyst particles substantially spherical in shape, i.e. with a very small ratio of surface to volume, or the particles would have to be very small. So far as industrial application is concerned, however, there

are limits to this on account of the high pressure loss involved.

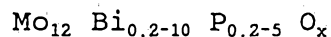
The catalysts produced and used by known methods have certain disadvantages in regard to the aspects mentioned. Elements of different shape are used with a view to shortening the diffusion paths, avoiding local overheating or achieving better utilization of the catalyst volumes by a suitable inner structure of the catalyst.

Hitherto, individual measures along these lines have resulted in comparatively unsatisfactory productivity per catalyst volume used where catalysts of the type in question are used in the industrial production of acrolein. This is a considerable economic disadvantage because, by way of compensation, large and expensive reactors with a high filling volume for the catalysts have to be used to carry out the reaction.

The object of the invention is to provide a catalyst for the production of unsaturated aldehydes from olefins, more particularly acrolein from propene, by oxidation with a gas containing molecular oxygen which, with a large ratio of geometric surface to volume and, at the same time, low diffusion resistance, overcomes these disadvantages and, in particular, provides for surprisingly high productivity.

The catalyst according to the invention is characterized by the following properties in combination:

- a) an active mass containing at least the elements molybdenum, bismuth, phosphorus and oxygen in atomic ratios of



and silicon-containing support material;

- b) a catalyst of any geometric shape in which the ratio of outer surface O_p to volume V_p is above 1.6 mm^{-1} and of which the spatial dimension, defined by the diameter of a sphere which still just surrounds it, is

smaller than 7.5 mm;

- c) a porosity of the catalyst element of at least 0.46, the absence of micropores (< 2 nm),
a mesopore volume (2 - 30 nm) of at least $0.03 \text{ cm}^3/\text{g}$ and preferably from 0.03 to $0.10 \text{ cm}^3/\text{g}$ and
a macropore volume (> 30 nm) of at least $0.30 \text{ cm}^3/\text{g}$ and preferably from 0.30 to $0.50 \text{ cm}^3/\text{g}$;
- d) a mercury density of the catalyst element of at least 1.25 g/cm^3 and preferably from 1.25 to 1.85 g/cm^3 ;
- e) a specific BET surface of at least $10 \text{ m}^2/\text{g}$ and preferably 10 to $25 \text{ m}^2/\text{g}$;
- f) a breaking strength of at least 6.0 N ;
- g) an abrasion of less 50 mg/g catalyst;
- h) a pressure loss of less than $1,600 \text{ Pa/m}$ of a catalyst bed introduced into a 2 cm diameter tube.

According to a further embodiment of the present invention there is provided a process for the production of the catalyst of the first embodiment, characterized in that

- a) a suspension of the co-precipitate obtained in known manner by combining salt solutions of the catalytically active elements (except Si) is mixed with the insoluble silicon-containing solid and the suspension obtained is spray-dried under conditions which provide for an initial temperature of the drying air of 300°C to 600°C , a temperature during deposition of the dried powder of 120°C to 220°C and a spraying intensity designed to produce a spray-dried powder having an average particle diameter of less than $30 \mu\text{m}$, the residence time of the spray-dried powder in the dryer being from 2 to 25 seconds,
- b) the spray-dried powder is calcined in a furnace, preferably a rotary kiln, over residence times of 5 to 60 minutes and at a peak temperature in the spray-dried powder of 320 to 480°C .
- c) the calcined spray-dried powder is extruded with 5 to 40% by weight, based on the quantity of spray-dried powder, of an pore-forming agent which decomposes completely at a temperature below 400°C and with wetting agents, lubricants and binders in a quantity sufficient to produce an extrudable mass, the wetting agents, lubricants and binders together making up to more than 40% .



TMS/1814R

by weight of the quantity of spray-dried powder, in the required geometric shape at a temperature below 80°C and under a pressure below 50 bar and the extruded strand is divided up by cutting to the length of the desired element,

- 5 d) the extruded individual elements are dried, the decomposable substance present is carefully removed by burning out in a furnace, preferably a rotary kiln, and the individual elements are conditioned in an air stream for 5 to 60 minutes at a peak temperature, as measured in the bed of individual elements, of 450
10 to 650°C.

The catalyst according to the invention affords major advantages in regard to volume-time yield in all mixed oxide formulations which are suitable for the relevant gas-phase oxidation and which contain at least molybdenum, bismuth and phosphorus in the claimed atomic ratios. The
15 activity required for a high volume/time yield is made possible by the favorable ratio between outer surface and volume and the favorable inner structure. By virtue of the increased ratio of surface to volume, the particular catalytically active mass is readily accessible to the reactants and the diffusion paths are short. The result of the favorable
20 inner structure is that the resistance to diffusion within the catalyst is minimal.

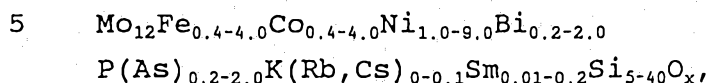
The high activity attributable to the large inner surface may thus be effectively utilized. Basically, the reduced resistance to diffusion in the catalyst element also has a favorable effect on selectivity.

- 25 The body of the catalyst according to the invention may have any geometric shape. Examples of preferred shapes are shown in the accompanying drawing.



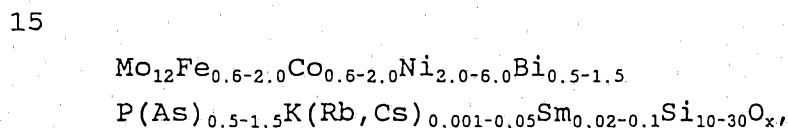
TMS/1814R

Of the catalyst formulations developed in the meantime which contain the basic constituents mentioned, a mass having the following composition:



the element silicon being present in the form of pyrogenic or highly disperse precipitated silica, silica sol, finely
 10 divided aluminium silicate and, more particularly, in the form of montmorillonite, has proved to be particularly suitable.

A preferred variant of this formulation consists of a mass having the following composition:



the element silicon being present in the form of pyrogenic
 20 SiO_2 and montmorillonite in a ratio by weight of 1:0.5 to 1:4.

It has proved to be appropriate in this regard for the montmorillonite to have a specific BET surface reduced by calcination of less than $2.0 \text{ m}^2/\text{g}$.

25 The present invention also relates to a process for the production of the described catalyst in its basic composition and the other variants which have been developed.

The process according to the invention is characterized in that

- 30 a) a suspension of the co-precipitate obtained in known manner by combining salt solutions of the catalytically active elements (except Si) is mixed with the insoluble silicon-containing solid and the suspension obtained is spray-dried under conditions which provide
 35 for an initial temperature of the drying air of 300°C

to 600°C, a temperature during deposition of the dried powder of 120°C to 220°C and a spraying intensity designed to produce a spray-dried powder having an average particle diameter of less than 30 μm , the residence time of the spray-dried powder in the dryer being from 2 to 25 seconds,

b) the spray-dried powder is calcined in a furnace, preferably a rotary kiln, over residence times of 5 to 60 minutes and at a peak temperature in the spray-dried powder of 320 to 480°C,

c) the calcined spray-dried powder is extruded with 5 to 40% by weight, based on the quantity of spray-dried powder, of an pore-forming agent which decomposes completely at a temperature below 400°C and with wetting agents, lubricants and binders in a quantity sufficient to produce an extrudable mass, the wetting agents, lubricants and binders together making up no more than 40% by weight of the quantity of spray-dried powder, in the required geometric shape at a temperature below 80°C and under a pressure below 50 bar and the extruded strand is divided up by cutting to the length of the desired element,

d) the extruded individual elements are dried, the decomposable substance present is carefully removed by burning out in a furnace, preferably a rotary kiln, and the individual elements are conditioned in an air stream for 5 to 60 minutes at a peak temperature, as measured in the bed of individual elements, of 450 to 650°C.

The process is based on a procedure which consists essentially of a combination of spray drying of the starting material under defined conditions, intermediate conditioning within the stated temperature range, extrusion of the calcined spray-dried powder with defined quantities of an pore-forming agent and typical processing aids in

limited quantities by weight under exact extrusion conditions and final conditioning in air at a raised temperature level. In one favorable embodiment of the process according to the invention, solid pentaerythritol having an average particle diameter of less 40 μm is used as the pore-forming agent. In addition to pentaerythritol, cellulose powder, urea, oxalic acid and polyvinyl alcohol may be used as the pore-forming agent.

Spray drying of the suspension of the co-precipitate under the stated conditions results in the formation of spherical spray-dried particles of high inner porosity. The high inner surface required for such catalysts is produced in this way. The intermediate conditioning step removes all decomposable constituents from the primary particles so that no reduction in strength can occur during the final conditioning step.

Under the effect of the pore-forming agent added during the extrusion step, preferably in the same particle size range as the primary particles, a macropore system is formed during the final conditioning step, making the highly reactive mesoporous primary particles readily accessible to the reactants. Petroleum or water may advantageously be used as lubricant during the extrusion step while a 1 to 10% by weight aqueous methyl cellulose solution, preferably in the form of an oil-in-water emulsion, may advantageously be used as wetting agent and binder or lubricant or dry methyl cellulose powder may advantageously be used as binder.

The final conditioning step at 450 to 650°C includes preliminary careful burning out during heating. However, the burning out and conditioning of the extruded individual elements may also be carried out in separate steps. In both cases, particularly good results are obtained if the extruded individual elements and the air stream are moved in co-current during the burning out phase and if the

burning out phase is carried out at a temperature of at most 400°C.

Where the new catalysts are used for the oxidation of olefins to unsaturated aldehydes by means of a gas containing molecular oxygen, for example in the preferred production of acrolein from propene, it is possible to establish very favorable operating conditions which lead to high productivity. The reaction is carried out at a temperature of 300 to 380°C and under a pressure of 1.4 to 2.2 bar. The reactants propene, air, inert gas, water are delivered to the catalyst bed in a ratio of 1 : 6-9 : 3-12 : 0-5 for a specific load of 2 to 8 mol propene/dm³ catalyst bed/h. Instead of inert gas, it is preferred to use the waste gas from the reaction with the condensable constituents removed. Particularly good results are obtained with tube bundle reactors in which the tubes have an internal diameter of 16 to 25 mm.

The invention is illustrated in the following by Examples:

The variables cited in the Examples are determined as follows:

1) Determination of porosity:

Porosity is calculated from the mercury and helium density in accordance with the following equation:

$$\text{porosity} = (1 - \text{Hg density}/\text{He density}) \cdot 100$$

(dimensionless)

"Porosity" is the percentage empty volume of the catalyst mass in relation to its overall volume.

2) Determination of mesopore volume:

Barrett, E.P.; Joyner, L.G.; Halenda, P.P.
J. Am. Chem. Soc., 73 (1951), page 373.

3) Determination of macropore volume:

Hg injection process using a Carlo-Erba 200 porosi-

meter up to 1,000 bar pressure.

- 4) Determination of bulk density, mercury density (apparent density) and helium density (true density):

5 Bulk density is determined by uniformly filling a straight steel tube having an internal diameter of 20 mm with 200 g catalyst in 1 minute and measuring the height of the resulting catalyst bed.

10 Mercury density is determined by introducing 2 g of the catalyst size-reduced to 200 μm into a pycnometer with a volume of 25 ml and then carefully filling the pycnometer with mercury. The mercury density (or apparent density) of the catalyst is obtained from the mass of the mercury required to fill the pycnometer with and without the catalyst sample and the mass of the catalyst sample itself. The helium density (or true density) of the catalyst mass is determined with a Beckmann air reference pycnometer.

- 15 20 5) Determination of BET surface in accordance with DIN 66 131 (measuring gas N_2):

Heating conditions: dried for 15 h at 100°C, degassed in vacuo for 1 h at 200°C.

- 25 6) Determination of breaking strength:
Breaking strength is measurement perpendicularly to the extrusion direction using an Erweka TBA 23, arithmetic mean of 100 individual measurements $\pm$ standard deviation.

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- 7) Determination of abrasion:

35 Abrasion is measured with a Roche TA3-R Friabilator, sample weight 50 g, 10 r.p.m., load application time 5 mins.; result expressed as abrasion of catalyst particles <1 mm in mg/g catalyst.

8) Determination of pressure loss:

Catalyst is uniformly introduced for 1 minute into a tube having an internal diameter of 2 cm, which is closed at its lower end by a wire gauze, in such a quantity that the height of the catalyst bed is 1 m. Air at 20°C is then passed through the catalyst bed at a rate of 1 Nm³/h and the pressure loss is measured.

9) Determination of particle size distribution:

Particle size distribution is measured with a CILAS 715 granulometer. Ethanol is used as the suspension liquid. To destroy agglomerates, ultrasound is applied for 1 minute.

10) Determination of catalytic properties:

The catalytic effect of the finished catalysts is tested in the reaction of propene to acrolein in an industrial tube reactor with an internal diameter of 20.5 mm externally cooled by a salt bath (length of catalyst bed 250 cm). The reaction is carried out with an input of 5.8 mol propene/h (or 5.2 mol propene/h, marked with an asterisk in Table 3), 43.5 mol air/h, 34.8 mol waste gas (composition: 5% O₂, 1% propene, 94% inert gas (CO₂, CO, N₂, Ar, propane)) and 2.9 mol H₂O/h and under a pressure of 1.8 bar at the entrance to the catalyst bed. The salt bath temperature adjusted, the maximum over-temperature obtained (exotherms) in the middle of the tube and the measured conversions and yields are shown in Table 3.

The acrolein yield (%) is defined as

$$\frac{\text{mol/h acrolein formed}}{\text{mol/h propene introduced}} \cdot 100$$

The acrylic acid yield (%) is defined as

$$\frac{\text{mol/h acrylic acid formed}}{\text{mol/h propene introduced}} \cdot 100$$

The conversion of propene (%) is defined as

$$\frac{\text{mol/h of propene issuing from the reaction tube}}{\text{mol/h propene introduced into the reaction tube}} \cdot 100$$

The acrolein selectivity (%) is defined as

$$\frac{\text{acrolein yield}}{\text{propene conversion}} \cdot 100$$

The acrylic acid selectivity (%) is defined as

$$\frac{\text{acrylic acid yield}}{\text{propene conversion}} \cdot 100$$

The acrolein productivity is defined as

$$\frac{\text{g/h acrolein formed}}{\text{dm}^3 \text{ catalyst bed}}$$

The following Examples relate to the production and use of the catalysts listed in Table 1.

The catalyst composition shown under Example No. 1 in Table 1, which is already described in DE-PS 11 29 150, was produced in geometric form III shown in Fig. 1.

Example 1

The co-precipitate for the production of the active catalyst phase is obtained by introducing 4,918 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 2,299 g H_2MoO_4 and 134 g 85% H_3PO_4 in 3,330 g water, to which 460 g conc. HNO_3 has been added, with

vigorous stirring at room temperature. The suspension formed is introduced into 6,338 g of an aqueous 30% silica sol suspension. The suspension is diluted with 4,250 g water and dried in a spray dryer at an entry temperature of the drying air of 500°C. The ratio of the quantity of drying air to the quantity of suspension sprayed is adjusted to give a residence time of 6 seconds of the spray-dried powder in the spray dryer. The spraying intensity is selected so that a spray-dried powder having an average particle diameter $\bar{d}_p$ of 6 μm is obtained.

The spray-dried powder is calcined in a rotary kiln for 60 minutes at a maximum temperature in the spray dried powder of 350 .

1.5 kg of the calcined powder are introduced into a combined kneader/extruder and mixed for 5 minutes with 0.375 kg pentaerythritol ("very finely ground") having an average particle diameter $\bar{d}_p$ of 40 μm . 600 g of a 10% tylose solution in which 100 g petroleum have been emulsified are then added to the resulting mixture. The mass is then kneaded until a homogeneous plastic state is reached. The plastic mass is then extruded under a pressure of 10 bar and at a temperature in the extruded mass of 20°C. The extruded hollow strand is cut at 5 mm intervals and the rings obtained (diameter 5 mm, length 5 mm, internal diameter 1.8 mm) are dried at room temperature.

The dried rings are introduced into a heated rotary kiln and are heated at a rotational speed of 2 min^{-1} in the presence of excess air to a peak temperature of 550°C in the bed passing through the rotary kiln. The residence time in the rotary kiln is 60 minutes.

The physical properties of the catalyst composition and its intermediate stages are shown in Table 2 while the effect of the catalyst in the production of acrolein is shown in Table 3. Comparison Example 1 below describes how the catalyst composition of DE-PS 11 29 150 is shaped in

the usual way to 5 x 5 mm tablets.

Comparison Example 1

5 The co-precipitate for the production of the active catalyst phase is produced in the same way as described in Example 1. The suspension obtained is concentrated by evaporation in vacuo to dryness in a rotary evaporator. The dry residue is size reduced and sieved through a 1 mm sieve. 5% by weight stearic acid as tableting aid are mixed with the powder obtained. The mixture is shaped in
10 a tableting machine to 5 x 5 mm tablets. The tablets are conditioned for 16 h at 538°C in a recirculating air drying cabinet into which fresh air is additionally introduced.

15 The catalyst composition shown under Example No. 2 in Table 1 was produced as follows in geometric form III of Fig. 1:

Example 2

20 The co-precipitate for the production of the active catalyst phase is obtained by dissolving 484.8 g $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$, 291.0 g $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, 1,163.2 g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 2.5 g KNO_3 in 3.1 l water and adding a solution of 17.4 g Sm_2O_3 in 106 g conc. HNO_3 with stirring at 90°C. 601 g highly disperse silica (Aerosil 200) and 1,202 g conditioned montmorillonite (specific BET surface
25 $<1 \text{ m}^2/\text{g}$) are added to the resulting solution with continued stirring. A solution of 2,118.6 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ in 2.7 l H_2O is prepared in a separate vessel at 60°C and 92.2 g 85% H_3PO_4 are added with intensive stirring to the solution thus prepared.

30 The two solutions are then combined with intensive stirring and a solution of 242.5 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 204 g 8.2% HNO_3 is added to the combined solutions. The suspension obtained is dried in a spray dryer at an entry temperature of the drying air of 550°C. The ratio of the
35 quantity of drying air to the quantity of suspension

sprayed is adjusted to give an exit temperature of 170°C and the quantity of suspension is gauged to give a residence time of 6 seconds of the spray-dried powder in the spray dryer. The spraying intensity is selected so that spray-dried powder having an average particle diameter $\bar{d}_p$ of 25 μm is obtained. The spray-dried powder is calcined in a rotary kiln for 30 minutes at a maximum temperature in the spray dried powder of 420°C.

1.6 kg of the calcined spray-dried powder are introduced into a combined kneader/extruder and mixed for 5 minutes with 0.4 kg pentaerythritol ("very finely ground") having an average particle diameter $\bar{d}_p$ of 40 μm . 493 g of a 6% by weight tylose solution in which 26.6 g petroleum have been emulsified are then added to the resulting mixture. The mass is then kneaded until a homogeneous plastic state is reached. The plastic mass is then extruded under a pressure of 10 bar and at a temperature in the extruded mass of 30°C. The extruded hollow strand is cut at 5 mm intervals and the rings obtained (diameter 5 mm, length 5 mm, internal diameter 1.8 mm) are carefully dried at 80°C.

The dried rings are introduced into a heated rotary kiln and are heated at a rotational speed of 2 min^{-1} in the presence of excess air to a peak temperature of 600°C in the bed passing through the rotary kiln. The residence time in the rotary kiln is 30 minutes.

The physical properties of the catalyst composition and its intermediate stages are shown in Table 2 while the effect of the catalyst in the production of acrolein is shown in Table 3.

In Example 3, the same catalyst composition as in Example 2 was produced in geometric form VI of Fig. 2.

Example 3

As in Example 2, the co-precipitate of the active

catalyst phase is produced, dried, calcined and kneaded in a combined kneader/extruder until a homogeneous plastic state is reached. The plastic mass is extruded under a pressure of 15 bar and at a temperature of 32°C in the extruded mass. The hollow strand extruded in form VI of Fig. 2 is cut at 5 mm intervals and the catalyst blanks thus obtained are dried and conditioned in a rotary kiln as in Example 2.

In Example 4, the same catalyst composition as in Example 2 was produced in geometric form II of Fig. 1.

Example 4

As in Example 2, the co-precipitate of the active catalyst phase is produced, dried, calcined and kneaded in a combined kneader/extruder until a homogeneous plastic state is reached. The plastic mass is extruded under a pressure of 15 bar and at a temperature of 32°C in the extruded mass. The hollow strand extruded in form II of Fig. 1 is cut at 5 mm intervals and the catalyst blanks thus obtained are dried and conditioned in a rotary kiln as in Example 2.

In Comparison Example 2, the same catalyst composition as in Example 2 was extruded in the form of strands.

Comparison Example 2

As in Example 2, the co-precipitate of the active catalyst phase is produced, dried, calcined and kneaded in a combined kneader/extruder until a homogeneous plastic state is reached. The plastic mass is extruded under a pressure of 8 bar and at a temperature of 25°C in the extruded mass. The catalyst mass extruded in form of a solid strand 5 mm in diameter is cut at 5 mm intervals and the catalyst blanks thus obtained are dried and conditioned in a rotary kiln as in Example 2.

In Examples 5, 6 and 7 below, various catalyst com-

positions are produced in geometric form III of Fig. 1 as in Example 2.

Example 5

The co-precipitate for the production of the active catalyst phase is obtained by dissolving 242.4 g
5 $\text{Fe}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$, 232.8 g $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, 1,744.8 g
 $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 5.1 g KNO_3 in 3.1 l water and adding a
solution of 34.9 g Sm_2O_3 in 212 g conc. HNO_3 with stirring
at 90°C. 300.5 g highly disperse silica (Aerosil 200) and
10 300.5 g conditioned montmorillonite (specific BET surface
<1 m²/g) are added to the resulting solution with continued
stirring. A solution of 2,118.6 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ in 2.7
l H_2O is prepared in a separate vessel at 60°C and 115.3 g
85% H_3PO_4 are added with intensive stirring to the solution
15 thus prepared. The two solutions are then combined with
intensive stirring and a solution of 485.1 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$
in 408 g 8.2% HNO_3 is added to the combined solutions. The
suspension obtained is dried in a spray dryer at an entry
temperature of the drying air of 550°C. The ratio of the
20 quantity of drying air to the quantity of suspension
sprayed is adjusted to give an exit temperature of 170°C
while the quantity of suspension is gauged to give a
residence time of 6 seconds of the spray-dried powder in
the spray dryer. The spraying intensity is selected so
25 that a spray-dried powder having an average particle
diameter $\bar{d}_p$ of 25 μm is obtained. The spray-dried powder
is calcined in a rotary kiln for 30 minutes at a maximum
temperature in the spray dried powder of 420°C.

The calcined spray-dried powder is further processed
30 as in Example 2, except for the fact that the extruded
hollow strand has an internal diameter of 2 mm.

Example 6

The co-precipitate for the production of the active
35 catalyst phase is obtained by dissolving 808.0 g

Fe(NO₃)₃ · 9 H₂O, 320.1 g Co(NO₃)₂ · 6 H₂O, 1,744.8 g
Ni(NO₃)₂ · 6H₂O and 0.1 g KNO₃ in 3.1 l water and adding a
solution of 34.9 g Sm₂O₃ in 212 g conc. HNO₃ with stirring
at 90°C. 600.9 g highly disperse silica (Aerosil 200) and
1,201.8 g conditioned montmorillonite (specific BET surface
<1 m²/g) are added to the resulting solution with continued
stirring. A solution of 2,118.6 g (NH₄)₆Mo₇O₂₄ · 6H₂O in 2.7
l H₂O is prepared in a separate vessel at 60°C and 115.3 g
85% H₃PO₄ are added with intensive stirring to the solution
thus prepared. The two solutions are then combined with
intensive stirring and a solution of 485.1 g Bi(NO₃)₃ · 5H₂O
in 408 g 8.2% HNO₃ is added to the combined solutions. The
suspension obtained is dried in a spray dryer at an entry
temperature of the drying air of 550°C. The ratio of the
quantity of drying air to the quantity of suspension
sprayed is adjusted to give an exit temperature of 170°C
while the quantity of suspension is gauged to give a
residence time of 6 seconds of the spray-dried powder in
the spray dryer. The spraying intensity is selected so
that a spray-dried powder having an average particle
diameter $\bar{d}_p$ of 25 μ m is obtained. The spray-dried powder
is calcined in a rotary kiln for 30 minutes at a maximum
temperature in the spray dried powder of 420°C.

The calcined spray-dried powder is further processed
as in Example 5.

Example 7

The co-precipitate for the production of the active
catalyst phase is obtained by dissolving 646.4 g
Fe(NO₃)₃ · 9 H₂O, 174.6 g Co(NO₃)₂ · 6 H₂O, 1,744.8 g
Ni(NO₃)₂ · 6H₂O and 0.1 g KNO₃ in 3.1 l water and adding a
solution of 34.9 g Sm₂O₃ in 212 g conc. HNO₃ with stirring
at 90°C. 600.9 g highly disperse silica (Aerosil 200) and
1,201.8 g conditioned montmorillonite (specific BET surface
<1 m²/g) are added to the resulting solution with continued

stirring. A solution of 2,118.6 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 6\text{H}_2\text{O}$ in 2.7 l H_2O is prepared in a separate vessel at 60°C and 115.3 g 85% H_3PO_4 are added with intensive stirring to the solution thus prepared. The two solutions are then combined with
5 intensive stirring and a solution of 727.7 g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 612.0 g 8.2% HNO_3 is added to the combined solutions. The suspension obtained is dried in a spray dryer at an entry temperature of the drying air of 550°C . The ratio of the quantity of drying air to the quantity of suspension
10 sprayed is adjusted to give an exit temperature of 170°C while the quantity of suspension is gauged to give a residence time of 6 seconds of the spray-dried powder in the spray dryer. The spraying intensity is selected so that a spray-dried powder having an average particle
15 diameter $\bar{d}_p$ of $25 \mu\text{m}$ is obtained. The spray-dried powder is calcined in a rotary kiln for 30 minutes at a maximum temperature in the spray dried powder of 420°C .

The calcined spray-dried powder is further processed in the same way as in Example 5.

20 The same catalyst composition as in Example 2 is shaped in Example 8, except for the fact that, in Example 8, pentaerythritol is replaced by cellulose powder as the pore-forming agent.

25 Example 8

The calcined spray-dried powder is produced as in Example 2.

30 1.6 kg of the calcined spray-dried powder are introduced into a combined kneader/extruder and mixed for 5 minutes with 0.4 kg cellulose powder, average particle diameter $\bar{d}_p = 36 \mu\text{m}$, as pore-forming agent.

The mixture is further processed as in Example 2.

In comparison Example 3, the catalyst is produced in the same way as in Example 2, except that no pore-forming
35 agent is added during the shaping process.

Comparison Example 3

The calcined spray-dried powder is produced in the same way as in Example 2.

5 1.6 kg of the calcined spray-dried powder are introduced into a combined kneader/extruder. 394.4 g of a 6% by weight tylose solution in which 21.3 g petroleum have been emulsified are then added. The mass is kneaded until a homogeneous plastic state is reached. The plastic mass
10 obtained is extruded in form III of Fig. 1 under a pressure of 14 bar and at a temperature of 32°C in the extruded mass.

The extruded mass is further processed in the same way as in Example 2, except that the peak temperature during conditioning in the rotary kiln is increased to 620°C.

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89 177 KY

Table 1 Catalyst composition (atomic numbers)

Examples	Comp. Ex.	Mo.	Fe	Co	Ni	Bi	P	K	Sm	Si (as montmorillonite + high disp. silica)
1	1	12	-	-	-	10.1	1.2	-	-	30
2,3,4,8	2,3	12	1.2	1.0	4.0	0.5	0.8	0.025	0.1	30
5		12	0.6	0.8	6.0	1.0	1.0	0.05	0.2	10
6		12	2.0	1.1	6.0	1.0	1.0	0.001	0.2	30
7		12	1.6	0.6	6.0	1.5	1.0	0.001	0.2	30

Table 2 Physical/chemical characterization of the catalysts

Ex.	Comp. Ex.	O_p/V_p mm^{-1}	d_K^* mm	Porosity -	V_{meso} ml/g	V_{macro} ml/g	Bulk g/ml	He- g/ml	Hg density g/ml	BET surf. m^2/g	Breaking strength N	Abrasion mg/g	Δp Pa/m
1		1.65	7.1	0.60	0.04	0.46	0.71	3.97	1.58	13	6.8	42	1440
	1	1.2	7.1	0.34	0.10	0.17	1.09	4.04	2.60	19	26.9	56	1620
2		1.65	7.1	0.51	0.05	0.38	0.76	3.48	1.71	14	14.9	16	1450
3		2.00	7.1	0.62	0.05	0.48	0.60	3.49	1.30	16	9.8	32	1400
4		2.10	7.1	0.62	0.04	0.42	0.70	2.54	1.30	16	15.4	48	1340
	2	1.2	7.1	0.64	0.04	0.42	0.79	3.59	1.30	16	18.9	20	1520
5		1.73	7.1	0.56	0.03	0.39	0.70	4.02	1.77	12	6.2	8	1260
6		1.73	7.1	0.56	0.04	0.30	0.72	4.05	1.79	11	10.7	4	1190
7		1.73	7.1	0.56	0.03	0.29	0.73	4.08	1.81	12	7.7	14	1290
8		1.65	7.1	0.62	0.04	0.33	0.76	3.51	1.30	16	14.4	18	1430
	3	1.65	7.1	0.44	0.05	0.25	0.87	3.46	1.93	13	16.8	11	1400

* d_K = diameter of the sphere in which the catalyst can still just fit

Table 3 **Effect of the catalysts in the production of acrolein**

Ex.	Comp. Ex.	Salt bath temp. °C	Conversion %	Exotherms °	Acrol. yield %	Acrylic acid Yield %	Acrol. select. %	Acrylic acid select. %	Productivity g acrol./ dm ³ catal./h
1		431	84.0	36	56.1	5.7	66.8	6.8	221
	1	422	82.5	38	50.9	5.2	61.7	6.3	180*
2		331	94.2	81	81.8	7.0	86.8	7.4	322
3		347	93.4	78	81.4	7.3	87.1	7.8	320
4		345	92.7	76	80.9	7.1	87.2	7.7	318
	2	330	93.1	78	77.6	8.5	83.3	9.1	273*
5		364	91.1	72	80.3	8.7	88.1	9.5	316
6		344	90.9	76	80.1	9.0	88.1	9.9	315
7		359	91.3	72	80.3	8.8	87.9	9.6	316
8		348	92.6	77	80.4	6.9	86.8	7.5	317
	3	350	90.0	74	77.1	6.0	85.6	6.7	272*

* Input 5.2 mol propene/h

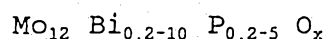
**A catalyst for the catalytic gas-phase oxidation of
olefins to unsaturated aldehydes**

—claims—

The claims defining the invention are as follows:

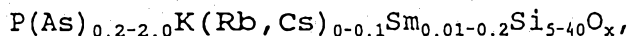
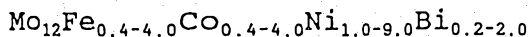
1. A catalyst for the production of unsaturated aldehydes from olefins, more particularly acrolein from propene, by oxidation with a gas containing molecular oxygen, characterized by the following properties in combination:

- 5 a) an active mass containing at least the elements molybdenum, bismuth, phosphorus and oxygen in atomic ratios of



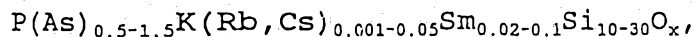
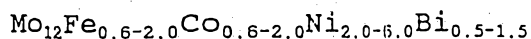
- 10 and silicon-containing support material;
- b) a catalyst element of any geometric shape in which the ratio of outer surface O_p to volume V_p is above 1.6 mm^{-1} and of which the spatial dimension, defined by the diameter of a sphere which still just surrounds it, is
- 15 smaller than 7.5 mm;
- c) a porosity of the catalyst of at least 0.46, the absence of micropores ($< 2 \text{ nm}$), a mesopore volume ($2 - 30 \text{ nm}$) of at least $0.03 \text{ cm}^3/\text{g}$ and
- 20 a macropore volume ($> 30 \text{ nm}$) of at least $0.30 \text{ cm}^3/\text{g}$;
- d) a mercury density of the catalyst element of at least 1.25 g/cm^3 ;
- e) a specific BET surface of at least $10 \text{ m}^2/\text{g}$;
- f) a breaking strength of at least 6.0 N;
- 25 g) an abrasion of less 50 mg/g catalyst;
- h) a pressure loss of less than 1,600 Pa/m of a catalyst bed introduced into a 2 cm diameter tube.

2. A catalyst as claimed in claim 1, characterized by a mass having the composition:



the element silicon being present in the form of pyrogenic or highly disperse precipitated silica, silica sol, finely divided aluminium silicate and, more particularly, in the form of montmorillonite.

3. A catalyst as claimed in claim 2, characterized by a mass having the following composition:



the element silicon being present in the form of pyrogenic SiO_2 and montmorillonite in a ratio by weight of 1:0.5 to 1:4.

4. A catalyst as claimed in claim 2 or 3, characterized in that the montmorillonite has a specific BET surface reduced by calcination of less than $2.0 \text{ m}^2/\text{g}$.

5. A process for the production of the catalyst claimed in any one of claims 1 to 4, characterized in that

a) a suspension of the co-precipitate obtained in known manner by combining salt solutions of the catalytically active elements (except Si) is mixed with the insoluble silicon-containing solid and the suspension obtained is spray-dried under conditions which provide for an initial temperature of the drying air of 300°C to 600°C , a temperature during deposition of the dried powder of 120°C to 220°C and a spraying intensity designed to produce a spray-dried powder having an average particle diameter of less than $30 \mu\text{m}$, the residence time of the spray-dried powder in the dryer being from 2 to 25 seconds,

b) the spray-dried powder is calcined in a furnace, preferably a rotary kiln, over residence times of 5 to

60 minutes and at a peak temperature in the spray-dried powder of 320 to 480°C,

- 5 c) the calcined spray-dried powder is extruded with 5 to 40% by weight, based on the quantity of spray-dried powder, of an pore-forming agent which decomposes completely at a temperature below 400°C and with wetting agents, lubricants and binders in a quantity sufficient to produce an extrudable mass, the wetting agents, lubricants and binders together making up no more than 40% by weight of the quantity of spray-dried powder, in the required geometric shape at a temperature below 80°C and under a pressure below 50 bar and the extruded strand is divided up by cutting to the length of the desired element,
- 10
- 15 d) the extruded individual elements are dried, the decomposable substance present is carefully removed by burning out in a furnace, preferably a rotary kiln, and the individual elements are conditioned in an air stream for 5 to 60 minutes at a peak temperature, as measured in the bed of individual elements, of 450 to 650°C.
- 20
6. A process as claimed in claim 5, characterized in that solid pentaerythritol having an average particle diameter of less than 40 μm is used as the pore-forming agent.
- 25 7. A process as claimed in claim 5 or 6, characterized in that petroleum or water is used as the lubricant and a 1 to 10% by weight aqueous methyl cellulose solution, preferably in the form of an oil-in-water emulsion, is used as the wetting agent and binder or lubricant or dry methyl cellulose powder is used as the binder.
- 30 8. A process as claimed in any one of claims 5 to 7, characterized in that burning out and conditioning of the extruded individual elements are carried out in separate steps.
- 35 9. A process as claimed in any one of claims 5 to 8, characterized in that the extruded individual elements and the air stream

are moved in co-current during the burning-out step and the burning-out step is carried out at a temperature of at most 400°C.

10. A catalyst for the production of unsaturated aldehydes from olefins substantially as hereinbefore described with reference to any one of the Examples.

11. A process for the production of a catalyst for the production of unsaturated aldehydes from olefins substantially as hereinbefore described with reference to any one of the Examples.

12. The product of the process of any one of claims 5 to 9.

DATED this FOURTH day of September 1990

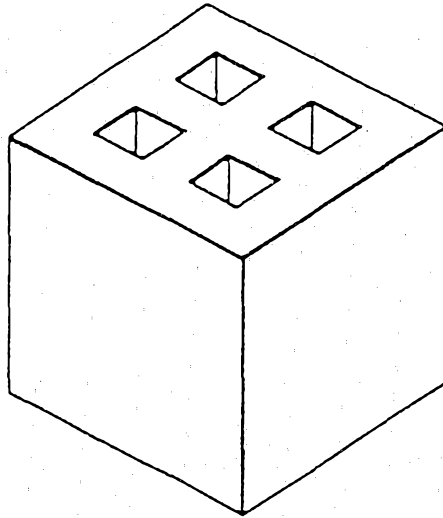
Degussa Aktiengesellschaft

Patent Attorneys for the Applicant

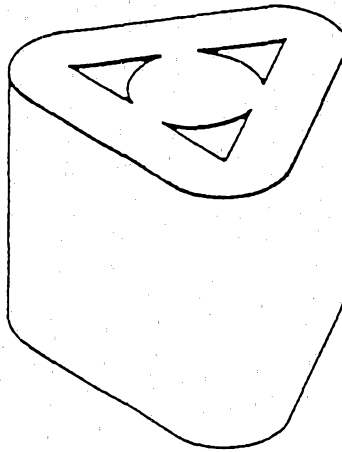
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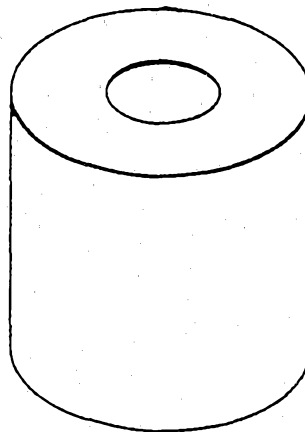
Fig. 1



I

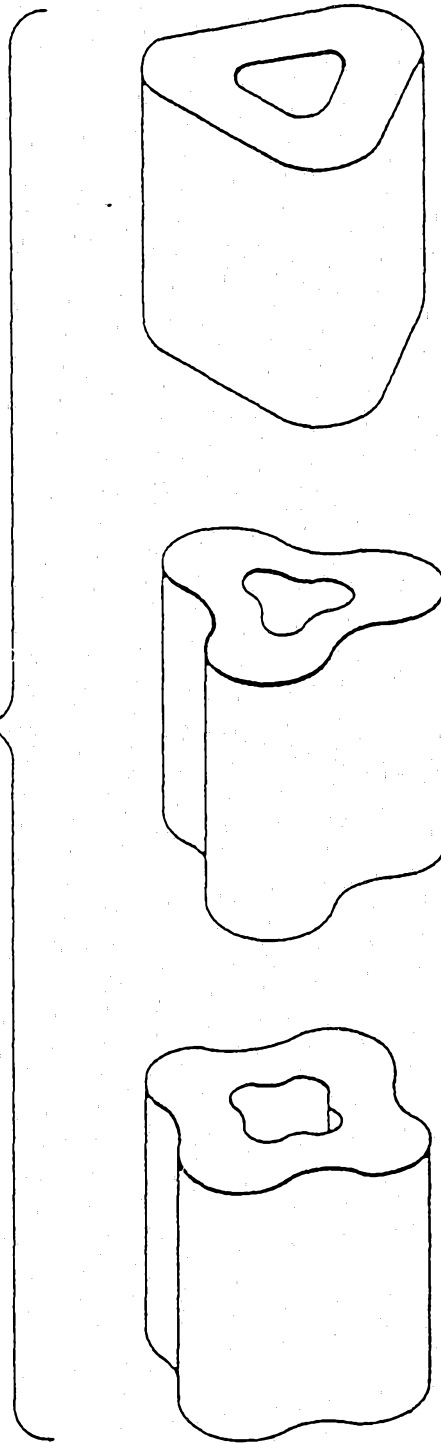


II



III

Fig. 2



IV

V

VI