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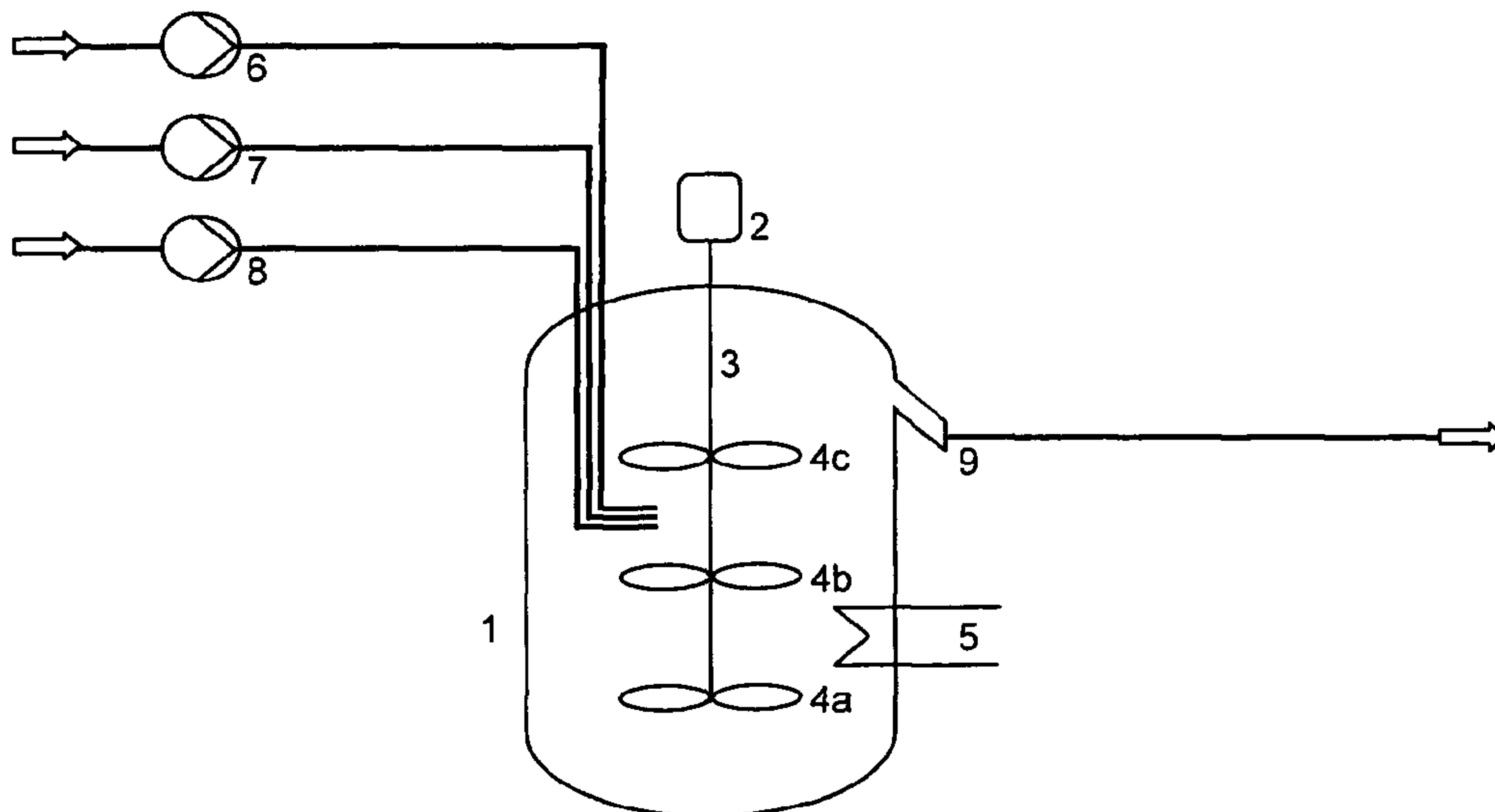
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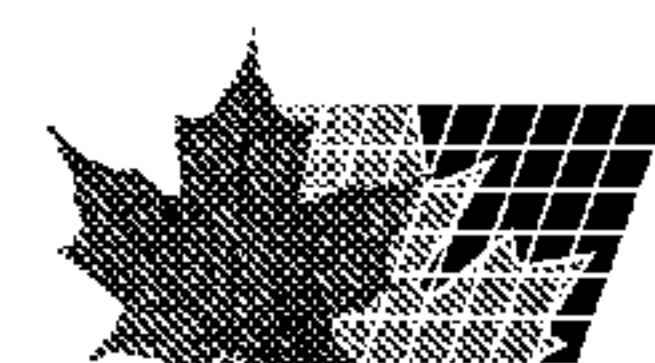
(54) **Titre : COMPOSES PULVERULENTS, LEURS PROCEDES DE PREPARATION ET LEUR UTILISATION DANS DES APPLICATIONS ELECTROCHIMIQUES**

(54) **Title: PULVERULENT COMPOUNDS, PROCESSES FOR THE PREPARATION THEREOF AND THE USE THEREOF IN ELECTROCHEMICAL APPLICATIONS**



(57) **Abrégé/Abstract:**

The present invention relates to pulverulent compounds of the formula $\text{Ni}_b\text{Ml}_c\text{M2}_d(0)_x(\text{OH})_y(\text{SO}_4)_z$, a process for the preparation thereof and the use thereof as precursors for the preparation of active materials for lithium secondary batteries.



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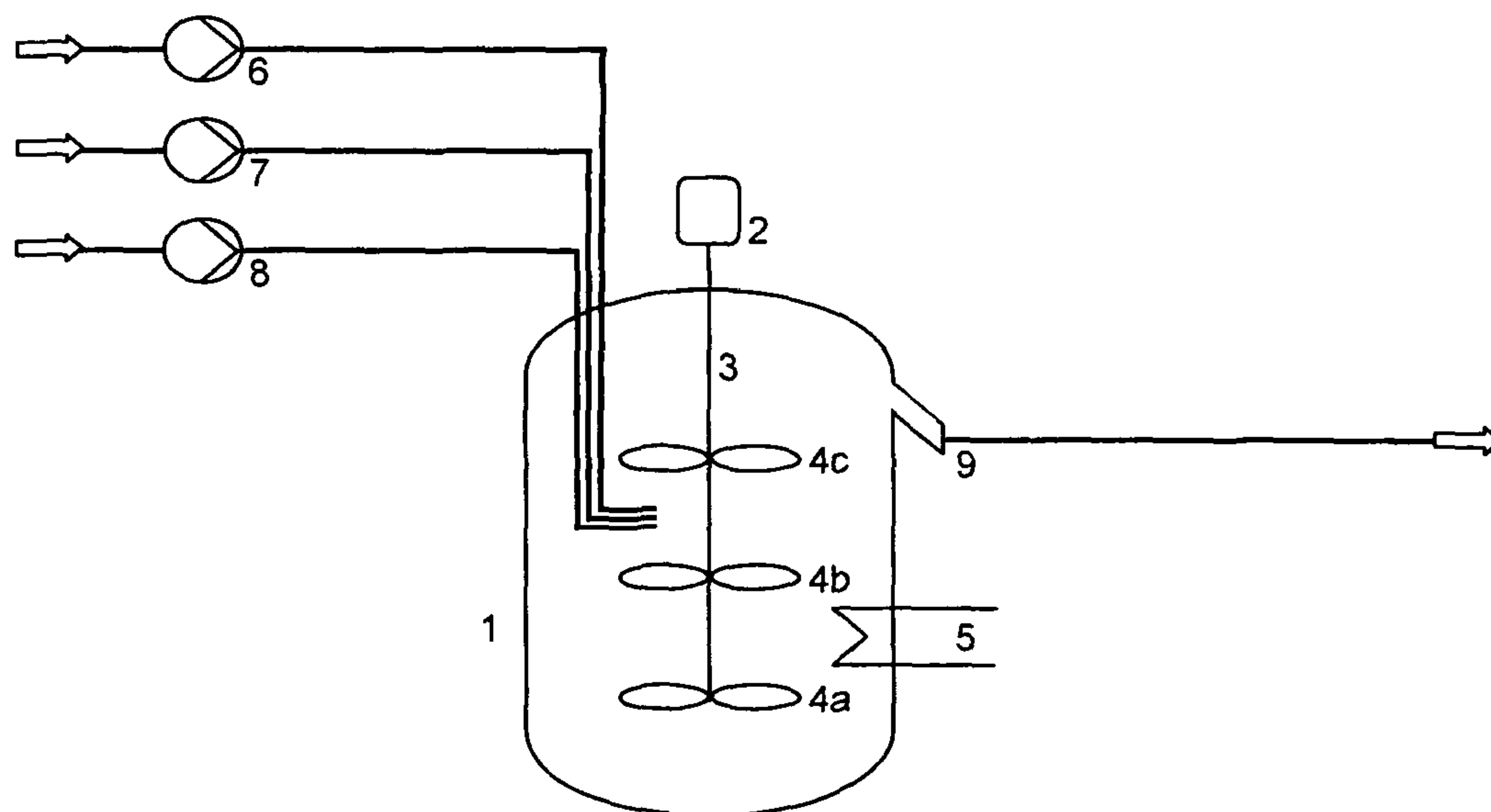
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(57) Abstract: The present invention relates to pulverulent compounds of the formula $\text{Ni}_b\text{Ml}_c\text{M2}_d(0)_x(\text{OH})_y(\text{SO}_4)_z$, a process for the preparation thereof and the use thereof as precursors for the preparation of active materials for lithium secondary batteries.

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Pulverulent compounds, processes for the preparation thereof and the use thereof in electrochemical applications

- 5 The present invention relates to pulverulent compounds of the formula $\text{Ni}_b\text{M1}_c\text{M2}_d(\text{O})_x(\text{OH})_y(\text{SO}_4)_z$, a process for the preparation thereof and the use thereof as a precursor for electrochemical applications.
- 10 A multiplicity of different doped or coated nickel compounds has been investigated and synthesized for a very long time in order to use them either as active material for NiMH batteries or as a precursor for a very wide range of lithium mixed metal oxides. Examples of
- 15 such compounds are coprecipitated hydroxides, such as an $\text{Ni}_{0.50}\text{Co}_{0.20}\text{Mn}_{0.30}(\text{OH})_2$, described in US 2002/0053663 A1, or an $\text{NiCo}(\text{OH})_2$ coated with $\text{Al}(\text{OH})_3$, as described in EP1637503A1.
- 20 The lithium mixed metal oxides synthesized from the nickel-containing precursor serve, in addition to the lithium cobalt oxide already in use for a relatively long time, as active cathode material for lithium ion secondary batteries. Under this very high energy density,
- 25 this type of secondary battery currently dominates the battery market with regard to mobile electronic devices, such as mobile phones, laptops or digital cameras.

Example compounds of such lithium mixed metal oxides are

30 $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ or $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.32}\text{O}_2$. Coprecipitated as well as coated nickel compounds are particularly suitable as precursors for the lithium mixed metal oxides, since a homogeneous distribution of the individual elements can be achieved as early as the stage

of the precursor. Homogeneous distribution of all metallic elements of the end product is of very great importance for the product properties in the battery.

- 5 At the required, high energy density of the storage media (NiMH batteries as well as lithium ion secondary batteries), a distinction may be made between the volumetric energy density, expressed in watt hours/litre (Wh/l), and the gravimetric energy density, expressed in
- 10 Wh/kg. The volumetric energy density of the secondary battery is influenced, inter alia, by the electrode density (g/cm^3) both on the side of the cathode and on the side of the anode. The higher the electrode density of the cathode or anode, the higher is the volumetric
- 15 energy density of the storage medium. The electrode density in turn is influenced both by the production process of the electrode and by the active cathode material used. The higher the density of the cathode material (for example, determined as tapped density or as
- 20 compressed density), the higher is the resulting electrode density under otherwise constant conditions during electrode manufacture (e.g. process for electrode manufacture, electrode composition). This discovery is already reflected in some documents. For the density of
- 25 the lithium mixed metal oxides as cathode material for lithium secondary batteries, the density of the corresponding precursor (e.g. a coprecipitated Ni(OH)_2 or a coated Ni(OH)_2) also plays an important role.
- 30 Since a certain pressure is applied during the electrode preparation, the tapped density or compacted density determined for the powder need not necessarily, however, permit direct conclusions about the electrode density with the use of this powder. The compressed density of a

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powder, determined under a defined pressure, is a variable which permits more reliable conclusions about an electrode density with this powder. A precondition of the abovementioned measurement of the compressed density as well as for the electrode manufacture should be that the particles do not break during the compression. Breaking of the particle would firstly mean uncontrolled manufacture of the electrode and furthermore such breaking of the particle would lead to inhomogeneities. Thus, the internal fracture surfaces of the broken particle would not have such good contact with the binder and the conductive additive of the electrode as the outer surface of the particles. US 2004/0023113 A1 is concerned with the determination of the compressed density and compressive strength of cathode powders.

Substances of the general formula $\text{Li}_x\text{M}(1-y)\text{N}_2\text{O}_2$ are mentioned therein as active cathode material for lithium secondary cells, where $0.2 \leq x \leq 1.2$ and $0 \leq y \leq 0.7$. Here, M is a transition metal and N is a transition metal differing from M, or an alkaline earth metal. In US 2004/0023113 A1, particular value is placed on the fact that the particle size distribution must have a defined form in order for the compression flow through the particle bed during the compression for electrode manufacture to be particularly gentle, and that the density of the electrode can also be optimized thereby. In addition to the particle size distribution, it is also mentioned that the particles of the powder should have pores which are as small as possible, and the pore volume of the pores up to a diameter of $1 \mu\text{m}$ should not exceed a value of $0.03 \text{ cm}^3/\text{g}$ (measured by Hg porosimetry). However, no particular process engineering measures are described for achieving said product parameters. In the

determination of the compressed density, the powder is pressed under a pressure of 0.3 t/cm^2 .

5 In the examples, mainly lithium cobalt oxides are described. At the abovementioned compression pressure of 0.3 t/cm^2 , compressed densities in the range of $2.58\text{--}3.32 \text{ g/cm}^3$ are reached.

10 In addition to the compressed density itself, value is furthermore placed on the fact that, after compression of the material, the volume fraction of the particles smaller than $1 \mu\text{m}$ is not greater than 0.1% . A significant increase in the fine particles after the compression would indicate that particles are destroyed during the
15 application of pressure. Such a phenomenon would endanger the homogeneity of the electrode.

However, it is to be assumed that a pressure of 0.3 t/cm^2 does not correspond to the pressures which are actually
20 applied during the electrode manufacture. During the electrode manufacture, the material must be capable of withstanding at least a pressure of 1 t/cm^2 . In JP 2001-80920 A a pressure of 2 t/cm^2 is stated in Example 1 for the electrode manufacture.

25 JP 2001-80920 A mentions the compressive strength of lithium mixed metal oxides (LNCO) which contain three metallic components in relation to lithium and can likewise be used as active materials for lithium
30 secondary batteries.

The materials thus manufactured have a compressive strength of $0.001\text{--}0.01 \text{ N}$. According to this document, it is desirable for the particles to disintegrate into their

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primary constituents during the electrode manufacture, which is contrary to the argumentation of US 2004/0023113 A1. According to JP 2001-80920 A, the material which has disintegrated into smaller constituents must have a certain flowability in order for the particles to be able to become uniformly distributed on the electrode.

US 2005/0220700 A1 likewise discusses the compressive strength of lithium mixed metal oxides. There, the compounds have the formula $\text{Li}_p\text{Ni}_x\text{Co}_y\text{Mn}_z\text{M}_q\text{O}_{2-a}\text{F}_a$. While only a value of 0.3 t/cm^2 is stated for the compressive strength in US 2004/0023113 A1, compressive strengths of at least 50 MPa, which corresponds to 0.5 t/cm^2 , are stated in US 2005/0220700 A1 for the lithium mixed metal compounds. However, the formula for the relevant compounds in US 2005/0220700 A1 is substantially more narrowly defined than that in US 2004/0023113 A1. Thus, manganese is a fixed constituent of all compounds in US 2005/0220700 A1. US 2005/0220700 A1 does not go into any detail as to why the compounds mentioned have a particular compressive strength. Only a defined particle size range and a defined range for the specific surface area of the materials are mentioned. No process engineering peculiarities which make the material particularly pressure-resistant are mentioned.

It is evident that the properties of the nickel-containing precursor for LNCO synthesis will also influence the compressive strength of the end product. It is to be assumed that a more pressure-resistant precursor also gives a more pressure-resistant end product. Parameters in the precursor, such as, for example, the porosity or the external shape of the particles, play a

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major role and also subsequently influence the compressive strength of the end product.

5 However, the documents mentioned provide no information about the compressive strength of the nickel-containing precursors for LNCO synthesis.

10 As already mentioned, both doped and coated nickel hydroxides are used not only as a precursor for LNCO synthesis but also directly as active material for NiMH batteries. In this application, too, a certain compressive strength is required.

15 The document JP 2002-304992 mentions the compressive strength of nickel hydroxides which are used as active material in secondary alkaline batteries. A primary aim of the document is to prepare a nickel hydroxide having improved performance data and improved high-temperature properties. Within the scope of this object, it was found
20 that the internal structure of the particles, and hence also the compressive strength of the particles, influence the performance data and the high-temperature properties of the nickel hydroxide. According to the document, the high internal, radial order of the particles is necessary
25 in order to be able to achieve good performance characteristics. This internal, radial order just mentioned is associated with a low compressive strength. Thus, according to the present document, the maximum compressive strength, measured on the individual particle
30 using an MCTM-200 apparatus from Shimadzu, of not more than 40 MPa is desirable for the nickel hydroxides.

BRIEF DESCRIPTION OF THE DRAWINGS

In the appended drawings:

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Figure 1 is a scheme of a reactor for the preparation of the nickel hydroxides according to the invention;

Figure 2 is a scanning electron micrograph of the product of Example 1;

5 Figure 3 is a scanning electron micrograph of the product of Example 1 after compression; and

Figure 4 shows the electrochemical behaviour of the nickel hydroxide in rechargeable nickel metal hydride test cells.

10 It is an object of the present invention to provide nickel-containing compounds as a precursor for

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electrochemical applications, in which the secondary particles are not broken or not comminuted during the further processing. Preservation of the secondary particles during the further processing is of great importance for the subsequent product homogeneity. At the same time, high electrode densities and good electrochemical properties in the end product should be achieved with such a nickel-containing precursor. It is furthermore the object of the present invention to provide a process for the preparation of a nickel-containing precursor.

The object is achieved by a pulverulent compound of the formula $\text{Ni}_b\text{M1}_c\text{M2}_d(\text{O})_x(\text{OH})_y(\text{SO}_4)_z$ (subsequently also referred to as NMOS, nickel hydroxide or mixed hydroxide), M1 denoting at least one element selected from the group consisting of Fe, Co, Cr, Mg, Cu and/or mixtures thereof, and/or M2 denoting at least one element selected from the group consisting of Mn, Al, B, Ca, Sr, Ba, Si, Zn and/or mixtures thereof and $0.3 \leq b \leq 0.94$, $0.02 \leq c \leq 0.5$, $0 \leq d \leq 0.5$ and $0.01 \leq x \leq 0.9$, $1.1 \leq y \leq 1.99$ and $0.001 \leq z \leq 0.03$, which is characterized in that the secondary particles thereof have a compressive strength of at least 50 MPa.

25

The secondary particles of the pulverulent NMOS compound preferably have a compressive strength of at least 100 MPa, particularly preferably at least 150 MPa. Compounds which are part of the invention are shown in Table 1.

30

Table 1

Compound	b	M1	c	M2	d	x	y	z
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1	0.333	Co	0.333	Mn	0.333	0.80	1.16	0.018
2	0.50	Co	0.20	Mn	0.30	0.75	1.22	0.015
3	0.77	Co	0.13	Mn	0.10	0.15	1.83	0.009
4	0.80	Co+Mg	0.10	Mn	0.10	0.11	1.88	0.007
5	0.70	Co	0.10	Mn+Zn	0.20	0.16	1.83	0.006
6	0.30	Co	0.30	Mn+Zn	0.40	0.65	1.32	0.015
7	0.80	Co	0.17	Al	0.03	0.02	1.97	0.005
8	0.75	Co+Fe	0.20	Al	0.05	0.03	1.96	0.006
9	0.93	Co	0.02	Zn	0.05	0.01	1.98	0.003
10	0.94	Co	0.02	Zn	0.04	0.01	1.99	0.002
11	0.60	Mg	0.10	Mn	0.30	0.10	1.89	0.004
12	0.45	Mg	0.10	Mn	0.45	0.20	1.78	0.009
13	0.333	Co	0.333	Mn	0.333	0.55	1.43	0.012
14	0.45	Co	0.10	Mn	0.45	0.50	1.48	0.009
15	0.40	Co+Mg	0.20	Mn	0.40	0.35	1.64	0.007
16	0.95	Co	0.02	Zn	0.03	0.01	1.98	0.003
17	0.60	Co	0.20	Mn	0.20	0.12	1.87	0.005
18	0.91	Co	0.02	Zn	0.07	0.02	1.97	0.004
19	0.92	Co	0.04	Zn	0.04	0.02	1.98	0.002
20	0.80	Co	0.16	Al	0.04	0.01	1.99	0.001
21	0.98	Co	0.024			0.01	1.98	0.003
22	0.91	Co	0.09			0.04	1.95	0.004
23	0.86	Co	0.14			0.06	1.92	0.003
24	0.81	Co	0.19			0.01	1.98	0.007

Secondary particles are understood as meaning compact particles which are composed of a multiplicity of primary particles which are readily visible in scanning electron micrographs. The particles may have any desired shape. The particles preferably have a spheroidal shape. Primary particles are particles which have formed from nuclei during a crystallization process.

The compressive strength of the secondary particles according to the invention can be determined by the method mentioned in US 2004/0023113 A1, page 6, Example 1.

5

The pulverulent nickel hydroxides according to the invention are distinguished by their very low porosity. According to the invention, the pulverulent nickel hydroxides have a porosity of up to $0.05 \text{ cm}^3/\text{g}$, preferably up to $0.04 \text{ cm}^3/\text{g}$, particularly preferably up to $0.03 \text{ cm}^3/\text{g}$. The porosity is determined according to ASTM D 4222.

The pulverulent nickel hydroxides according to the invention may be prepared both in spheroidal and in regular (nonspheroidal particle shape).

The preferred powders according to the invention are distinguished in particular by the spheroidal particle shape of the secondary particles, the shape factor of which has a value greater than 0.8, particularly preferably greater than 0.9.

The shape factor of the secondary particles can be determined by the method mentioned in US 5476530, columns 7 and 8 and Figure 5. This method determines a shape factor of the particle which is a measure of the sphericity of the particles. The shape factor of the secondary particle can also be determined from the scanning electron micrographs of the materials.

The shape factor is determined by evaluating the particle circumference and the particle area and determining the

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diameter derived from the respective size. The stated diameters are obtained from

$$d_U = U/\pi \qquad d_A = (4A/\pi)^{1/2}$$

5

The shape factor of the particles f is derived from the particle circumference U and the particle area A according to:

$$10 \quad f = \left(\frac{d_A}{d_U} \right)^2 = \left(\frac{4\pi A}{U^2} \right).$$

In the case of an ideal spherical particle, d_A and d_U are of equal magnitude, and a shape factor of exactly one would result.

15

Preferably, the pulverulent nickel hydroxides according to the invention have a D10 value, measured according to ASTM B 822, which changes by not more than 0.5 μm , preferably by not more than 1.0 μm , compared with the
20 starting powder after compression of the powders at a pressure of 50 MPa. The change in the D10 value as a result of the powder compression is considered to be an indicator for the assessment of the compressive strength of the pulverulent compound according to the invention
25 after compression.

A decrease in the D10 value after the compression means that a fraction of the particle was broken into smaller particles. Thus, the change in the D10 value is a
30 quantitative measure for determining the compressive strength of the powders according to the invention.

The pulverulent nickel hydroxides according to the invention have a normalized width of the particle distribution, measured according to the formula (1)

$$\frac{D90-D10}{D50} \quad (1)$$

in which D denotes diameters of the secondary particles, of less than 1.4, particularly preferably of less than 1.2.

The pulverulent lithium mixed metal oxides according to the invention preferably have a compressed density of at least 2.4 g/cm³.

The pulverulent nickel hydroxides according to the invention are also distinguished by the fact that they have a tapped density of at least 2.0 g/cm³, particularly preferably of at least 2.3 g/cm³, measured according to ASTM B527.

The invention furthermore relates to a novel process for the preparation of pulverulent metal hydroxides comprising the following steps:

- a. provision of starting material solutions,
- b. metering of starting material solutions from step a) into a reactor,
- c. reaction of the starting material solutions in a highly turbulent reaction zone of the reactor in which the flows produced by the stirrer strike one another frontally,
- d. discharge of the product suspension from the reactor via a free overflow,

e. filtration, washing and drying of the material.

Metal hydroxides from the group consisting of the metals such as Al, Ti, Zr, Hf, Fe, Co, Ni, Zn, Cu and Ag can be prepared by the process according to the invention. The starting materials used are starting material solutions of water-soluble salts of mineral acids, e.g. sulphuric acid, hydrochloric acid or nitric acid, with the abovementioned metals and/or mixtures thereof. The starting material solutions can be prepared by dissolving the relevant metal chlorides, metal solvates or metal nitrates in water or dissolving the metals in the corresponding mineral acids. The alkali solutions are provided in the desired concentration as an aqueous solution.

The process is preferably suitable for the preparation of nickel hydroxides according to the invention. Water-soluble metal salts, e.g. nickel sulphate, nickel nitrate, nickel halides, such as, for example chlorides or fluorides, and/or mixtures thereof can be used as precursors.

The preparation of the nickel hydroxides according to the invention is preferably carried out in a reactor (1) shown in Fig. 1, by precipitation crystallization from aqueous nickel salt solutions at a pH of 8-14, preferably of 9-13, by feeding in alkali metal hydroxide solutions and optionally ammonia, in gaseous form or as an aqueous solution. Preferably used alkali metal hydroxide solutions are sodium hydroxide and potassium hydroxide. Although the precipitation crystallization can be effected batchwise or semicontinuously, it is preferably carried out continuously. In the continuous process,

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metal salt solution, alkali metal hydroxide solution and ammonia solution are fed simultaneously to the reactor and the product suspension is taken up continuously via a free overflow or a pump.

5

Both the metering of starting material solutions and the production and maintenance of a highly turbulent reaction zone of the reactor play a very important role in the process according to the invention. For thoroughly mixing
10 the starting material solutions and achieving a homogeneous suspension, the reactor is equipped with a stirrer (2) with variable speed.

A peculiarity of the reactor used in the process
15 according to the invention is that three propellers (4a), (4b) and (4c) are arranged in various planes on a common centrally mounted stirrer shaft (3). It is possible to use multiblade propellers. However, the three-blade propellers are preferred. It was found that the
20 properties of the products are dependent on the introduction point of the starting material solutions in the reactor, the distance between the propeller planes and the angle of attack of the propeller blades. Pressure-resistant and dense nickel hydroxides according
25 to the invention can be prepared if the feed of the starting material solutions, subsequently also referred to as feed solutions, is effected in a zone between 2 propellers which produce the flows meeting one another. It was found that particularly pressure-resistant and
30 dense nickel hydroxide can be very uniformly prepared in a continuously operated reactor if the feed solutions are fed in-between the middle and upper propeller and, in the case of a propeller rotating in the mathematically positive sense (to the left) when viewed from above, the

angle of attack of the blades of the propeller relative to the horizontal stirrer plane of the upper and lower propeller is 30 to 60°, preferably 40 to 60°, particularly preferably 45 to 55°, and the angle of attack of the blades of the metal propeller is 120 to 150°, preferably 130 to 150°, particularly preferably 135 to 145°. In this configuration, the upper and lower propellers produce a downward flow and the middle propeller an upward flow. The feeding of the feed solutions between the upper and middle propeller thus takes place in a zone of particularly high turbulence, since 2 flows impact one another frontally there. The downward flow of the lower propeller prevents solid particles from being deposited on the bottom of the reactor. In order to ensure very thorough mixing of the feed solutions and a very homogeneous suspension in the reactor, the vertical arrangements of the 3 propellers relative to one another and to the height of fill of the reactor must be within certain ranges. Below, the heights of the lower, middle and upper propeller above the reactor bottom are designated by (a), (b) and (c) and the height of fill of the reactor by (h). It was found that particularly pressure-resistant and dense nickel hydroxides can be prepared if $0.1 \leq a/h \leq 0.3$ for the lower propeller, $0.4 \leq b/h \leq 0.6$ for the middle propeller and $0.7 \leq c/h \leq 0.9$ for the upper propeller. The ranges of $0.2 \leq a/h \leq 0.3$, $0.4 \leq b/h \leq 0.5$ and $0.7 \leq c/h \leq 0.8$ are particularly preferred. Depending on the specific object, such as, for example, density of the solid particles produced and mean particle diameter the angular velocity and diameter of the propellers can be chosen according to the known rules of technology. Thus, it is entirely possible for the propellers on the 3 different planes to have different diameters.

The particularly pressure-resistant nickel hydroxides according to the invention can be particularly advantageously prepared in the reactor described.

5

The invention furthermore relates to a reactor for carrying out precipitation reactions, which is characterized in that it comprises a stirrer which has 3 propellers in 3 different horizontal planes on a common shaft and in that one propeller produces a flow in the opposite direction to the other two propellers.

10

The pulverulent compounds according to the invention are suitable in particular as precursors for the preparation of active materials for lithium secondary batteries.

15

The invention is furthermore explained by the following examples and comparative examples.

20 **Examples**

The nickel hydroxides prepared in the following examples were investigated with regard to various physical properties, as stated in the examples. Unless noted otherwise, the procedure was as follows:

25

- D10, D50 and D90 values were measured according to ASTM B 822 by means of laser diffraction using a Master-Sizer S μ from MALVERN,
- 30 - BET (specific surface area) was determined according to ASTM D 3663,
- tapped density was determined according to ASTM B 527,
- porosity was determined according to ASTM D 4222.

The preparation of the product according to the invention was effected in the reactor (1) shown in Fig. 1 by precipitation crystallization from aqueous solution. For thoroughly mixing the starting material solutions and achieving a homogeneous suspension, the reactor is equipped with a stirrer (2) with variable speed. Three propellers (4a), (4b) and (4c) are arranged in various planes on a common shaft (3), the propellers (4a) and (4c) producing a downward flow, and an upward flow being produced by propeller (4b).

For establishing a constant temperature, the reactor is equipped with a regulated heat exchanger (5). The reactor is operated continuously by a procedure in which metal sulphate solution is continuously metered in by means of pump (6), ammonia solution by means of pump (7) and sodium hydroxide solution by means of pump (8), and the resulting suspension flows out of the reactor via the free overflow (9). This overflow ensures that the suspension volume is kept steady at 40 litres. Depending on the resulting volume flow of the suspension and hence the average residence time, or waiting time of up to 6 residence times was allowed in the experiments and then the suspension obtained within the next two residence times was collected for further working-up. The working-up was effected by filtration over a suction filter, washing with 2 litres of water, with 2 litres of dilute sodium hydroxide solution (1 g/l) and again with 2 litres of water per kg of product and subsequent drying over the filter cake on metal trays in a drying oven (with hot air) at 80°C to constant weight.

Example 1

The reactor (1) was operated at a temperature of 50°C and with a stirrer speed of 600 rpm. 2717 g/h of metal sulphate solution having a concentration of (109.6 g/l of Ni, 2.84 g/l of Co, 7.58 g/l of Zn), 143 g/h of ammonia solution (225 g/l of NH₃) and 1621 g/h of sodium hydroxide solution (274.6 g/l of NaOH) were metered in continuously. After the elapse of 50 h, the reactor had reached its steady state and the suspension then running out was collected over 20 h and worked up as described above. 8.01 kg of dry product of the formula $\text{Ni}_{0.9192}\text{Co}_{0.0238}\text{Zn}_{0.0570}\text{O}_{0.0101}(\text{OH})_{1.9839}(\text{SO}_4)_{0.0031}$ having a residual moisture content of 0.20% were obtained. The physical properties of the product are shown in Table 2. The electrochemical behaviour of the nickel hydroxide in rechargeable nickel metal hydride test cells is shown in Fig. 4. The relative charging capacity (% OES) of the one-electron step (Ni(II)→Ni(III)) is plotted against the number of cycles. Fig. 2 shows a scanning electron micrograph of the product.

20

5 g of the material obtained in Example 1 were exposed to a pressure of 50 MPa in a toggling press. The behaviour of the material is likewise shown in Table 2. Fig. 3 shows a scanning electron micrograph after compression.

25

Fig. 3 shows that the spheroidal secondary particles have substantially retained their shape after the compression and are not broken into fragments of spheroidal particles. This shows that a material bed of the compound presented here withstands a pressure of 50 MPa without the particles being broken.

30

Comparative Example 1

The experiment was carried out analogously to Example 1, with the only difference that the conventional reactor was used instead of the reactor (1) according to the invention. After the drying, 8.014 kg of product of the
5 formula $\text{Ni}_{0.9191}\text{Co}_{0.0238}\text{Zn}_{0.0571}\text{O}_{0.0203}(\text{OH})_{1.9712}(\text{SO}_4)_{0.0044}$ having a residual moisture content of 0.22% were obtained. The physical properties of the product are again shown in Table 1. The electrochemical utilization of the one-electron step in an NiMeH test cell is also shown in
10 diagram 1.

It is evident that the drop in the charging capacity after the maximum in the 2nd cycle is smaller in the case of the product according to the invention than in the
15 case of that prepared according to the prior art. In addition, the product according to the invention has a somewhat higher charging capacity. Experience shows that these trends measured in test cells continue with the use in batteries where charging and discharging are effected
20 over a few hundred cycles. Furthermore, owing to the higher tapped density and compressed density, the material according to the invention additionally has a higher volume capacity. This means that the advantage of the material according to the invention over the prior
25 art is even greater than shown in Fig. 4. The physical properties of the product are shown in Table 2.

5 g of the material obtained in Comparative example 1 were once again exposed to a pressure of 50 MPa in a
30 toggling press. The behaviour of the material is likewise shown in Table 2. The material has a high compressed density, and particle size distribution of the agglomerates changes only very slightly.

Example 2

The reactor (1) was operated at a temperature of 45°C and with a stirrer speed of 900 rpm. 1490 g/h of metal sulphate solution having a concentration of (40.81 g/l of Ni, 40.98 g/l of Co, 38.20 g/l of Mn), 95 g/h of an ammonia solution (225 g/h of NH₃) and 1010 g/h of sodium hydroxide solution (232.7 g/l of NaOH) were metered in continuously. After the elapse of 90 h, the reactor had reached its steady state and the suspension then running out was collected over 36 h and worked up as described. 8.005 kg of dry product of the formula $\text{Ni}_{0.3333}\text{Co}_{0.3334}\text{Mn}_{0.3333}\text{O}_{0.2101}(\text{OH})_{1.7744}(\text{SO}_4)_{0.0078}$ having a residual moisture content of 0.25% were obtained. The physical properties of the product are once again shown in Table 2.

5 g of the material obtained in Example 2 were once again exposed to a pressure of 50 MPa in a toggling press. The behaviour of the material is likewise shown in Table 2.

Comparative Example 2

The mixed hydroxyoxysulphate of the metals Ni, Co and Mn was prepared analogously to Example 2, but in a conventional stirred reactor. 7.995 kg of dry product of the formula $\text{Ni}_{0.3334}\text{Co}_{0.3333}\text{Mn}_{0.3333}\text{O}_{0.3011}(\text{OH})_{1.6811}(\text{SO}_4)_{0.0095}$ having a residual moisture content of 0.26% were obtained. The physical properties of the product are shown in Table 2.

5 g of the material obtained in Comparative Example 2 were once again exposed to a pressure of 50 MPa in a

toggling press. The behaviour of the material is likewise shown in Table 2.

With the material, it is not possible to achieve
5 compressed densities as high as those achieved with the
nickel hydroxide according to the invention. This is
because the comparative material already has a
substantially lower tapped density than the material
according to the invention which was prepared according
10 to Example 2. This difference is retained on pressing.

Table 2

	Example 1		Comparative Example 1		Example 2		Comparative Example 2	
	Originally	Compressed at 50 MPa	Originally	Compressed at 50 MPa	Originally	Compressed at 50 MPa	Originally	Compressed at 50 MPa
D ₁₀ [μm]	5.61	5.44	3.98	3.39	5.05	4.77	3.20	2.48
D ₅₀ [μm]	11.86	11.82	10.14	10.02	10.95	10.97	7.93	7.67
D ₉₀ [μm]	20.81	21.17	18.87	19.11	19.80	20.01	14.81	14.99
BET [m ² /g]	10.17		12.84		11.36		14.05	
Tapped density [g/cm ³]	2.33		2.15		2.08		1.78	
Compressed density [g/cm ³]		2.64		2.43		2.42		2.15
Porosity [cm ³ /g]	0.0232		0.0455		0.0296		0.051	

CLAIMS

1. Pulverulent compound of the formula $\text{Ni}_b\text{M1}_c\text{M2}_d(\text{O})_x(\text{OH})_y(\text{SO}_4)_z$,

M1 denoting Fe, Co, Cr, Mg, or Cu, or a mixture thereof,

M2 denoting Mn, Al, B, Ca, Sr, Ba, Si, or Zn, or a mixture thereof, and

$$0.3 \leq b \leq 0.94,$$

$$0.02 \leq c \leq 0.5,$$

$$0 \leq d \leq 0.5,$$

$$0.01 \leq x \leq 0.9,$$

$$1.1 \leq y \leq 1.99, \text{ and}$$

$$0.001 \leq z \leq 0.03,$$

the pulverulent compound being in the form of secondary particles having a compressive strength of at least 50 MPa, and

the pulverulent compound having a porosity of up to $0.03 \text{ cm}^3/\text{g}$, measured according to ASTM D 4222,

wherein a normalized width of the particle distribution, calculated using formula (1):

$$(\text{D}_{90} - \text{D}_{10}) / \text{D}_{50} \quad (1),$$

in which D denotes diameters of the secondary particles, is less than 1.4.

2. Pulverulent compound according to Claim 1, wherein the secondary particles have a compressive strength of at least 100 MPa.
3. Pulverulent compound according to Claim 2, wherein the secondary particles have a compressive strength of at least 150 MPa.
4. Pulverulent compound according to any one of Claims 1 to 3, wherein the secondary particles have a spheroidal shape.
5. Pulverulent compound according to Claim 4, wherein the secondary particles have a shape factor greater than 0.8.

6. Pulverulent compound according to any one of Claims 1 to 5, wherein a D10 value of the pulverulent compound, measured according to ASTM B 822, varies by not more than 0.5 μm upon compression at a pressure of 50 MPa.
7. Pulverulent compound according to any one of Claims 1 to 5, where a D90 value of the pulverulent compound, measured according to ASTM B 822, varies by not more than 1 μm upon compression at a pressure of 50 MPa.
8. Pulverulent compound according to any one of Claims 1 to 7, having a compressed density of at least 2.4 g/cm^3 at a compression pressure of 50 MPa.
9. Pulverulent compound according to any one of Claims 1 to 8, having a tapped density, measured according to ASTM B 527, of at least 2.0 g/cm^3 .
10. Pulverulent compound according to Claim 9, wherein the tapped density is of at least 2.3 g/cm^3 .
11. A process for the preparation of a pulverulent compound as defined in any one of claims 1 to 10, comprising the following steps:
 - a) providing starting material solutions, said starting material solutions being solutions of water-soluble salts of a mineral acid with a metal, the metal being Al, Ti, Zr, Hf, Fe, Co, Ni, Zn, Cu, Ag or a mixture thereof, or alkali solutions,
 - b) metering the starting material solutions into a reactor comprising a stirrer,
 - c) reacting the starting material solutions in a turbulent reaction zone in which flows produced by the stirrer strike one another frontally,
 - d) discharging a product suspension from the reactor via a free overflow, and
 - e) filtrating the pulverulent compound out of the product suspension, and washing and drying the pulverulent compound.
12. Process according to Claim 11, wherein the reactor comprises a centrally inserted stirrer shaft on which three propellers, namely an upper propeller, a middle propeller, and a lower propeller, are arranged in different planes.
13. Process according to Claim 12, wherein both the upper and the lower propellers produce a downward flow and wherein the middle propeller produces an upward flow.

14. Process according to Claim 12 or 13, wherein the propellers have three blades.
15. Process according to Claim 14, wherein the angle of attack of the blades of the upper and lower propellers relative to an horizontal stirrer plane is 30 to 60° and wherein the angle of attack of the blades of the middle propeller is 120 to 150° relative to the horizontal stirrer plane.
16. Process according to Claim 15, wherein the angle of attack of the blades of the upper and lower propellers relative to the horizontal stirrer plane is 45 to 55° and wherein the angle of attack of the blades of the middle propeller is 135 to 145° relative to the horizontal stirrer plane.
17. Process according to any one of Claims 12 to 16, wherein a vertical arrangement of the propellers relative to a height of fill of the reactor has the ratio:
$$0.1 \leq a/h \leq 0.3 \text{ for the lower propeller,}$$
$$0.4 \leq b/h \leq 0.6 \text{ for the middle propeller, and}$$
$$0.7 \leq c/h \leq 0.9 \text{ for the upper propeller,}$$

a, b, c denoting the heights of each propeller above the reactor bottom and h denoting the height of fill of the reactor.
18. Process according to Claim 17, wherein:
$$0.2 \leq a/h \leq 0.3 \text{ for the lower propeller,}$$
$$0.4 \leq b/h \leq 0.5 \text{ for the middle propeller, and}$$
$$0.7 \leq c/h \leq 0.8 \text{ for the upper propeller.}$$
19. Process according to any one of Claims 11 to 18, characterized in that the starting material solutions are metered in at a height between a height of the upper propeller and a height of the middle propeller.
20. Reactor for carrying out the process of any one of claims 11 to 19, the reactor containing a reaction vessel provided with a centrally inserted stirrer shaft on which three propellers, namely an upper propeller, a middle propeller, and a lower propeller, are arranged in different planes.

21. Reactor according to Claim 20, wherein both the upper and the lower propellers produce a downward flow and wherein the middle propeller produces an upward flow.
22. Reactor according to Claim 20 or 21, characterized in that the propellers have three blades.
23. Reactor according to Claim 22, wherein the angle of attack of the blades of the upper and lower propellers relative to a horizontal stirrer plane is 30 to 60° and wherein the angle of attack of the blades of the middle propeller is 120 to 150° relative to the horizontal stirrer plane.
24. Reactor according to Claim 23, wherein the angle of attack of the blades of the upper and lower propellers relative to the horizontal stirrer plane is 45 to 55° and wherein the angle of attack of the blades of the middle propeller is 135 to 145° relative to the horizontal stirrer plane.
25. Reactor according to any one of Claims 20 to 24, wherein a vertical arrangement of the propellers relative to a height of fill of the reactor has the ratio:
$$0.1 \leq a/h \leq 0.3 \text{ for the lower propeller,}$$
$$0.4 \leq b/h \leq 0.6 \text{ for the middle propeller, and}$$
$$0.7 \leq c/h \leq 0.9 \text{ for the upper propeller,}$$
a, b, c denoting the heights of each propeller above the reactor bottom and h denoting the height of fill of the reactor.
26. Reactor according to Claim 25, wherein:
$$0.2 \leq a/h \leq 0.3 \text{ for the lower propeller,}$$
$$0.4 \leq b/h \leq 0.5 \text{ for the middle propeller, and}$$
$$0.7 \leq c/h \leq 0.8 \text{ for the upper propeller.}$$
27. Use of a reactor as defined in one of Claims 20 to 26 for the preparation of a pulverulent compound as defined in any one of claims 1 to 10.
28. Pulverulent compound as defined in one of Claims 1 to 10, produced by the process of any one of Claims 11 to 19.

29. Use of a pulverulent compound as defined in any one of Claims 1 to 10 as a precursor for the preparation of an active material for lithium secondary batteries.
30. Use of a pulverulent compound as defined in any one of Claims 1 to 10 as an active material for nickel metal hydride batteries.

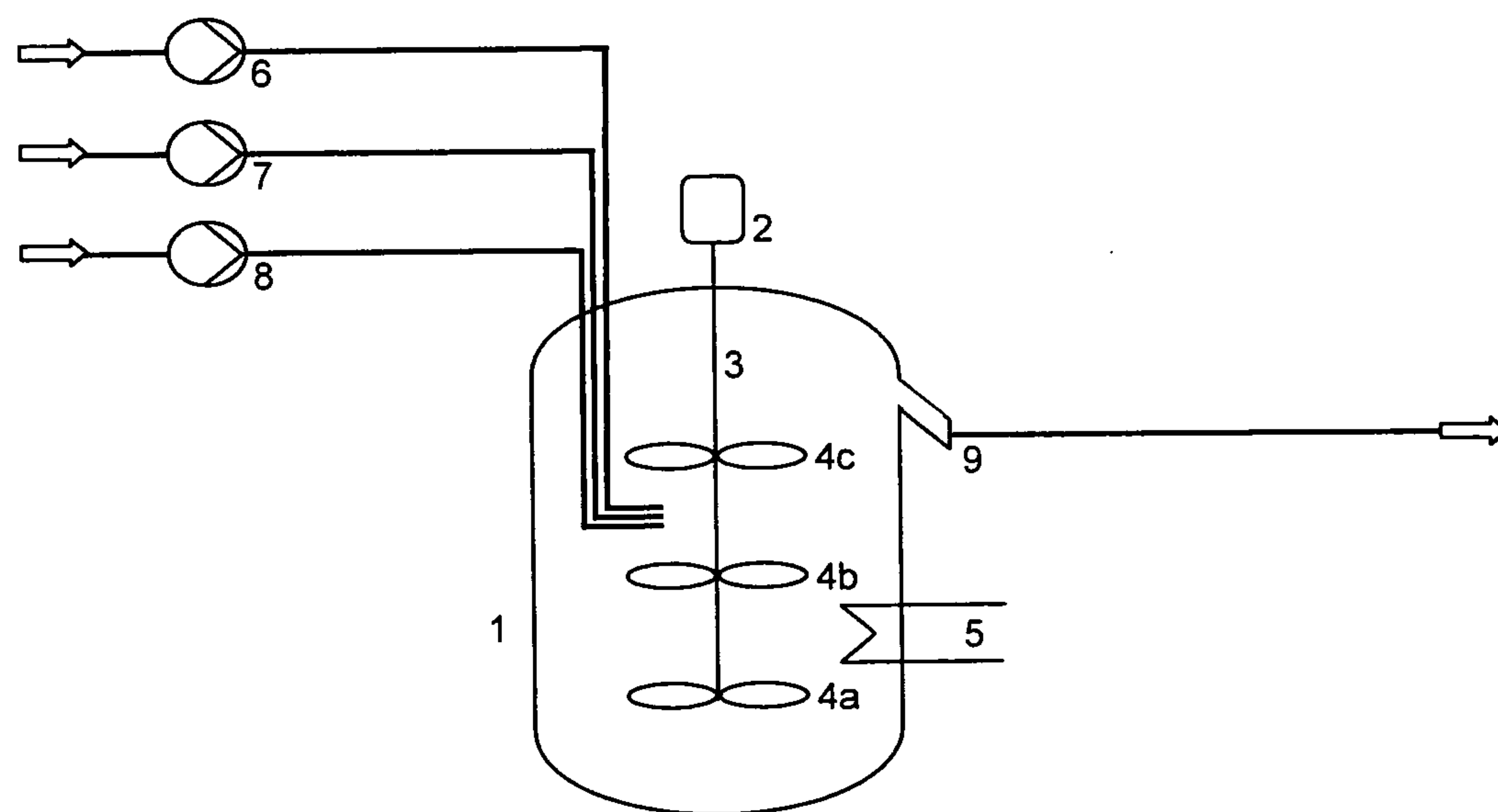


Fig. 1

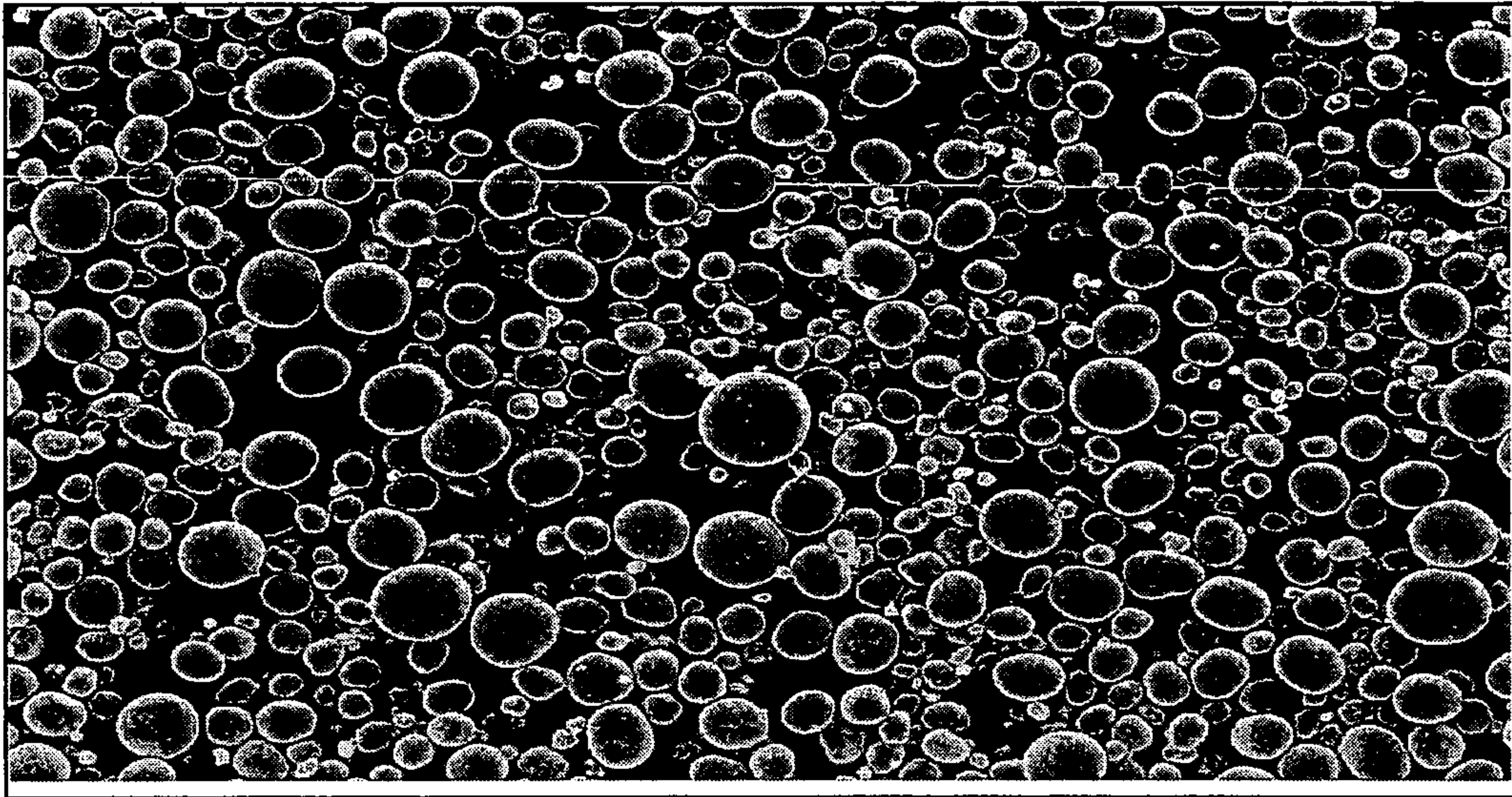


Fig. 2

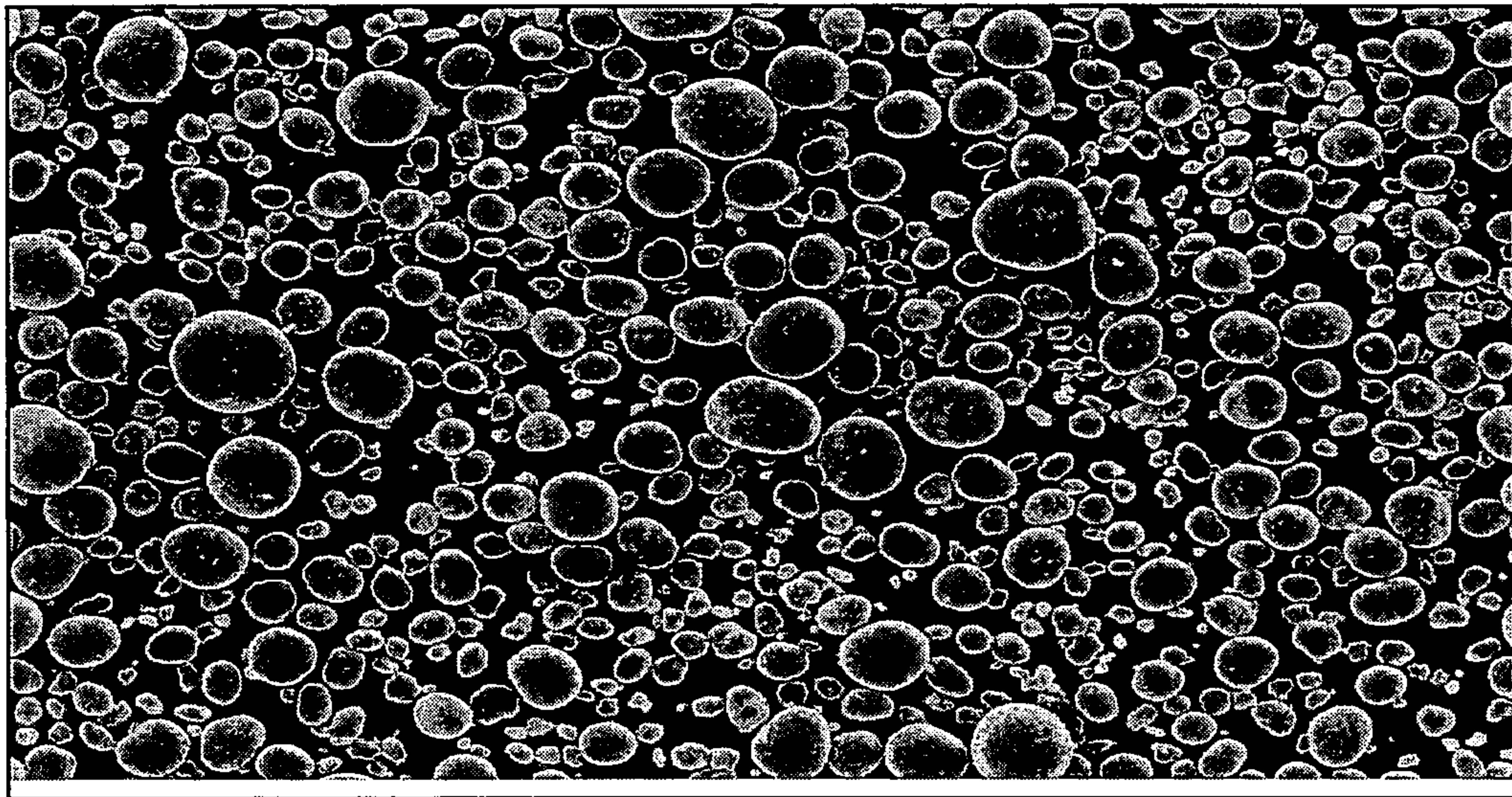
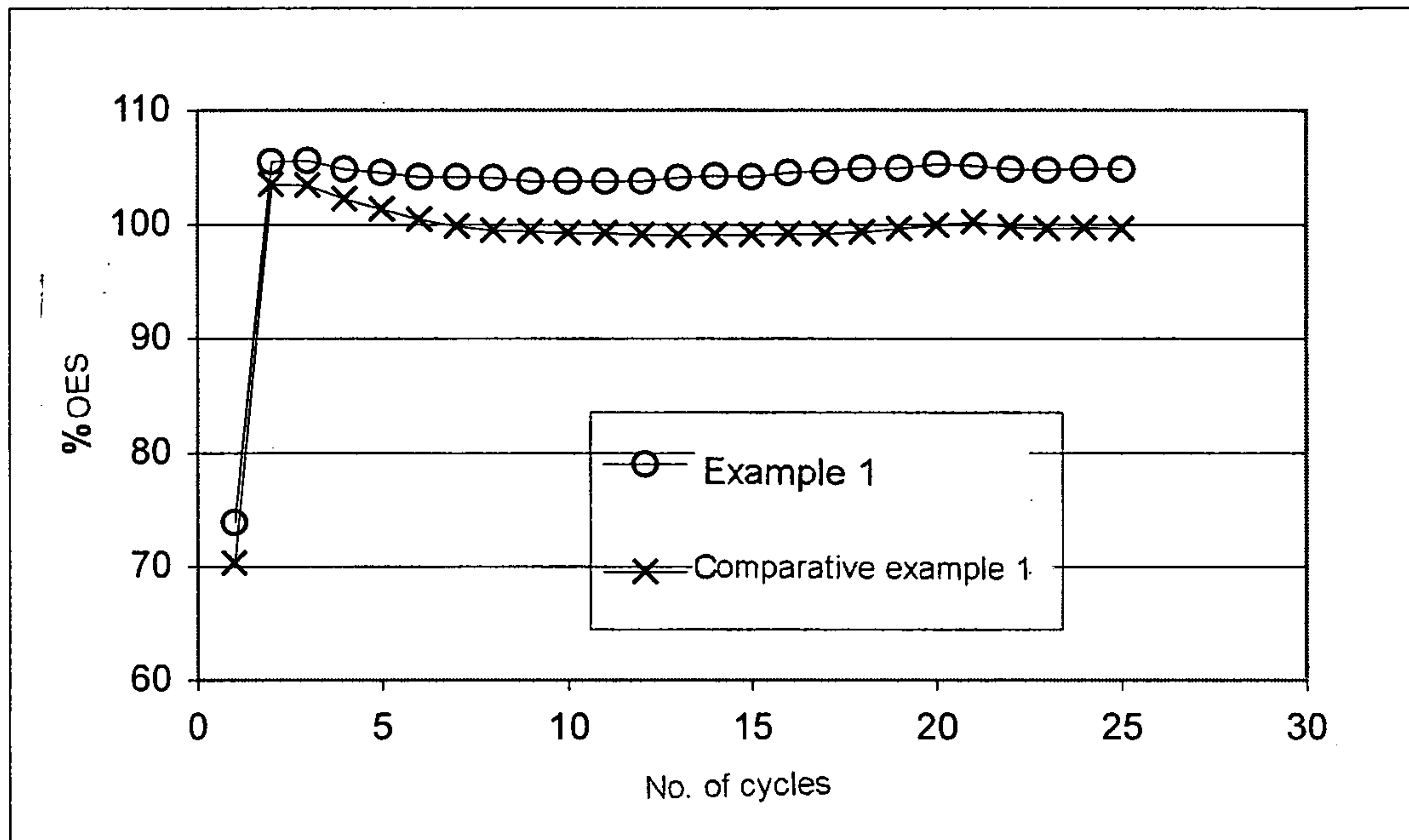


Fig. 3

**Fig. 4**

