

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:

Precipitant or Flocculant for Treatment of Waste Water
and Process Involving Their Use

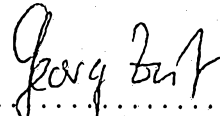
I, Dr Georg Zeit, of Falkenweg 2, 4018 Langenfeld, Federal Republic of Germany do solemnly and sincerely declare as follows:

1. I am authorised by Henkel Kommanditgesellschaft Auf Aktien, 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 Federal Republic of Germany on 14 November 1988 by Henkel Kommanditgesellschaft Auf Aktien.
3. Helmut Endres, Gunter Geismar and Angela Hansen, of Benrodestrasse 82, D-4000 Dusseldorf 13; Ratherstrasse 30, D-4150 Krefeld 1 and Kapitelstrasse 47, D-4040 Neuss 1 all in the Federal Republic of Germany, respectively, are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:-

The applicant is the assignee of the invention from the actual 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 the subject of the application.

DECLARED at Langenfeld this 29 day of May 1991

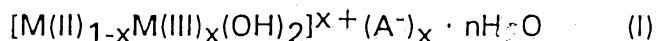

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Georg Zeit

TO: THE COMMISSIONER OF PATENTS
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PRECIPITANT OR FLOCCULANT FOR TREATMENT OF WASTE WATER AND PROCESS INVOLVING THEIR USE
- (51)⁵ International Patent Classification(s)
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- (56) Prior Art Documents
EP 560068
- (57) Claim

1. A precipitating or flocculating agent for waste water treatment, comprising double-layer hydroxides of the general composition (I)



wherein

M(II) is at least one divalent metal ion,

M(III) is at least one trivalent metal ion,

A is an equivalent of one or more mono- or polybasic acids,

x is between 0.01 and 0.5, and

n is between 0 and 20,

characterized in that the agent contains at least 30% by weight of hydrophilic solvents, and has solid particles with an average particle diameter of less than 2µm, and no particles with a particle diameter in excess of 10µm.

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(21) Internationales Aktenzeichen: PCT/EP89/01324 (22) Internationales Anmeldedatum: 6. November 1989 (06.11.89) (30) Prioritätsdaten: P 38 38 532.5 14. November 1988 (14.11.88) DE (71) Anmelder (für alle Bestimmungsstaaten ausser US): HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN [DE/DE]; Henkelstraße 67, D-4000 Düsseldorf-Holthausen (DE). (72) Erfinder; und (75) Erfinder/Anmelder (nur für US): ENDRES, Helmut [DE/DE]; Benrodestraße 82, D-4000 Düsseldorf 13 (DE). GEISMAR, Günter [DE/DE]; Ratherstraße 30, D-4150 Krefeld 1 (DE). HANSEN, Angela [DE/DE]; Kapitelstraße 47, D-4040 Neuss 1 (DE).	(81) Bestimmungsstaaten: AT (europäisches Patent), AU, BE (europäisches Patent), BR, CH (europäisches Patent), DE (europäisches Patent), DK, FI, FR (europäisches Patent), GB (europäisches Patent), IT (europäisches Patent), JP, LU (europäisches Patent), NL (europäisches Patent), NO, SE (europäisches Patent), US. Veröffentlicht <i>Mit internationalem Recherchenbericht. Vor Ablauf der für Änderungen der Ansprüche zugelassenen Frist. Veröffentlichung wird wiederholt falls Änderungen eintreffen.</i>	
(54) Title: PRECIPITANT OR FLOCCULANT FOR TREATMENT OF WASTE WATER AND PROCESS INVOLVING THEIR USE		
(54) Bezeichnung: FÄLLMITTEL ODER FLOCKUNGSMITTEL ZUR ABWASSERBEHANDLUNG UND VERFAHREN UNTER VERWENDUNG DIESER MITTEL		
(57) Abstract The invention concerns a precipitant or flocculant for purifying waste water, as defined in the description, characterized in that it contains a certain quantity of hydrophilic solvents such that the agglomeration of the primary particles to form secondary particles which are not precipitated in water is prevented and such that the average diameter of the particles in aqueous suspension is less than 2 µm and that no particles with a particle diameter greater than 10 µm are present. To obtain the product, either (a) the salts used as starting materials for the production of these double-layer hydroxides are introduced in equivalent amounts in a solvent into a common reactor, and the precipitated precipitant is used, possibly after washing with a solvent, in moist form without previous drying to a solids content greater than 70 wt. %, or (b) the precipitate is produced in situ by carrying out the above-mentioned steps in the waste water to be treated. Also described are the manufacture of the products and the process involving their use. (57) Zusammenfassung Die vorliegende Erfindung betrifft ein Fällmittel oder Flockungsmittel zur Abwasserreinigung, wie in der Beschreibung definiert, dadurch gekennzeichnet, daß es einen gewissen Anteil an hydrophilen Lösungsmitteln aufweist und so die Agglomeration der Primärteilchen zu in Wasser nicht zerfallenden Sekundärteilchen soweit verhindert wird, daß deren mittlerer Teilchendurchmesser in einer wäßrigen Suspension kleiner als 2 µm ist, und keine Teilchen mit einem Teilchendurchmesser von mehr als 10 µm vorhanden sind, und das erhältlich ist, indem man (a) entweder die als Ausgangsstoffe für die Herstellung dieser Doppelschicht-Hydroxide verwendeten Salze in zueinander äquivalenten Mengen in einem Lösungsmittel einem gemeinsamen Reaktionsort zuführt und nach der Fällung das Präzipitat, gegebenenfalls nach Waschen mit einem Lösungsmittel, in feuchter Form, ohne eine vorherige Trocknung über einen Feststoffgehalt von 70 Gew.-% hinaus, einsetzt oder (b) das Präzipitat in situ unter Berücksichtigung obiger Maßnahmen im zu behandelnden Abwasser erzeugt, ihre Herstellung und Verfahren unter Verwendung dieser Mittel.		

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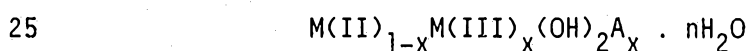
Precipitants or flocculants for waste water treatment and a
process using these precipitants or flocculants

The present invention relates to precipitants or flocculants for waste water treatment, more particularly for treating laundry waste waters. The invention also relates to processes using these agents.

Supplying industry and homes with fresh water is becoming increasingly more difficult. This applies to the conurbations of Central Europe and particularly to the arid areas of Southern Europe, the U.S.A., etc. The increased expenses for treating shore filtrates or even surface waters are reflected in increasing costs. Accordingly, it would seem advisable both for ecological reasons and for economic reasons to intensify the search for methods of recycling water by suitable reprocessing of waste water. This applies, for example, to laundries for which methods of saving fresh water have been discussed in the literature (for example E. Köppelmann, W.-A. Roland and H. Grund, "Möglichkeiten des Wasserrecyclings in Wäschereibetrieben (Possibilities of Recycling Water in Laundries)", Reiniger + Wäscher, Vol. 35, No. 5, 20-26 (1982)).

One of the goals of the invention is to provide a new precipitant or flocculant for treating waste water, more particularly laundry waste water. Another goal of the invention is to provide a waste water treatment process using these precipitants or flocculants.

For this purpose there are used freshly precipitated cationic stratified compounds having the following general composition



in which

- M(II) denotes a divalent metal ion,
M(III) denotes a trivalent metal ion,
30 A denotes an equivalent of an acid,
x assumes a value between 0.01 and 0.5 and
n assumes a value between 0 and 20,

and which are present in a special form described hereinafter.

The flocculation of substances responsible for turbidity in waste water using salts of trivalent metals, more particularly Fe(III) ions and Al(III) ions, is well-proved state of the art. There exists a large literature on the fundamentals of the relevant processes and their embodiments, cf. for example the book by Hermann H. Hahn:

"Wassertechnologie (Water Technology)", Springer-Verlag 1987, Chapter 4.

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The mechanism is assumed to be that, at the pH value of domestic waste water, the cited metal ions hydrolyze to render positively charged oligomeric hydroxy compounds and destabilize and flocculate the negatively charged suspended dirt by Coulomb interaction. By inclusion
5 in, or adsorption to, the flocs formed in this way, other waste water ingredients which are not suitable for flocculation can be removed. The separability of the dirt flocs is usually promoted by the addition of flocculation aids (organic polymers having various charge).

However, a disadvantage of these processes lies in the often
10 unsatisfactory separability of the flocs. This applies in particular where the problem to be solved is the removal of dirt from laundry waste water to facilitate the re-use of the purified water for laundry purposes. Even where polymeric flocculation aids are used, treatment with aluminium salts or iron salts often results in precipitates which
15 are difficult to filter and in a heavily clouded "clean water phase". For example, FR-A-24 66 438 claims a process for the purification of laundry waste water by addition of aluminium sulfate in quantities equal to the solids content of the waste water. Though, as Comparison Example 3 shows, favourable turbidity levels and low total
20 solids contents are obtained in this way, the filtered wash liquor still appears whitish and clouded to the naked eye. The acidic pH value is also unfavourable to recycling the wash liquor. A similar process uses polymeric aluminium salts, such as basic polychlorosulfates of aluminium, in conjunction with iron salts (EP-A-0 261 019).

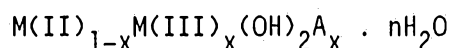
25 The use of solids with a stratified structure of an other kind has also been known for treating waste water. The compounds used in this case are either compounds having negative layer charges, such as, for example, the clay mineral bentonite (e.g., DE-AS 1 642 886, DE-OS 25 29 099), optionally in combination with sodium aluminate (DE-OS 36 31 472),
30 or compounds having substantially neutral layers, such as specially precipitated calcium hydroxide or magnesium hydroxide (for example DD-PS 1580 25). While bentonites preferentially adsorb positively charged contaminants by Coulomb interactions, the neutral hydroxides bind impurities, irrespective of their charge, by van der Waals interactions.
35 The same also applies to spatial lattice compounds, such as zeolites, the use of which was also suggested in this context (cf. the above-cited article by E. Köppelmann et al). Since, in the latter cases, there are no powerful electrostatic forces to support the binding process, the cleaning effect is not very pronounced. Comparison Example 2 illustrates



the effect of the stratified silicate bentonite on the wash liquor: the separability of the solid phases is inadequate.

By contrast, the problem addressed by the present invention is to effectively remove preferably negatively charged waste water ingredients, such as occur in particular in laundry waste waters (for example anionic surfactants and builders, but also the dirt particles which are negatively charged at the usual pH values of wash liquors). Layer compounds having a positive stratified charge are available as the reagent. Compounds such as these are known in the literature as "double layer hydroxides" (for example R. Allmann, "Doppelschichtstrukturen mit brucitähnlichen Schichtionen (Double-Layer Structures with Brucite-Like Layer Ions)", *Chimia* 24, 99-108 (1970)).

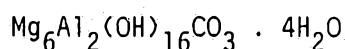
Chemically, they are mixed basic hydroxo salts of divalent and trivalent metal ions and may be characterized by the following general formula:



in which

- 20 M(II) denotes a divalent metal ion,
 M(III) denotes a trivalent metal ion,
 A denotes an equivalent of an acid,
 x assumes a value between 0.01 and 0.5 and
 n assumes a value between 0 and 20.

25 Some of the properties of this class of compounds, such as their use as a catalyst material, as an ion exchanger and certain medicinal applications, have been comprehensively described by W.T. Reichle ("Anionic Clay Minerals", CHEMTECH, Jan. 1986, pages 58-63). A well characterized representative of this group of compounds is hydrotalcite
30 which occurs as a mineral in nature, but which can also be synthesized. Hydrotalcite is a magnesium/aluminium hydroxycarbonate of the following approximate composition:



35 of which the structure was determined by X-ray diffraction analysis (R. Allmann and H.P. Jepsen, "Die Struktur des Hydrotalkits (The Structure of Hydrotalcite)", *N. Jahrb. Mineral. Monatsh.* 1969, pages 544-551). Compounds such as these have the major ecological advantage over organic



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flocculants that they are already present in the form of minerals and, accordingly, do not require biological degradation.

The use of powdery or pelletized hydrotalcite-like solids for water treatment has been described in some patent specifications.

5 According to Chemical Abstracts, Vol. 91, Abstract No. 216 265s (1979), which is a summary of JP-A-54/93854, phosphate-containing waste waters can be purified with a hydrotalcite-like chemical compound by virtue of its sorption and exchange properties.

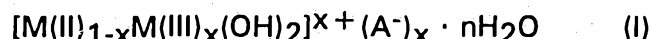
10 Chemical Abstracts, Vol. 103, Abstract No. 202 527h (1985), which is a summary of EP-A-0 152 010, describes a method for purifying cooling water of atomic reactors using a calcined hydrotalcite-containing solid.

Accordingly, it appeared logical at first sight to use such compounds for purifying laundry waste waters. However, if dried or powdered products are used for this purpose (Comparison Example 4), no advantage is obtained over 15 the above-mentioned solids known from the state of the art. The filtered wash liquor is heavily clouded.

Therefore, the problem underlying the present invention was to provide a novel precipitant or flocculant for treating waste water, more particularly laundry waste water, with which the waste water could be better purified and 20 which would lead to optically almost completely clear solutions.

It has now surprisingly been found that specially produced and humidified hydrotalcite minerals of the above-described type in paste-like form with a water content (as determined by drying for 4 h at 110°C) of at least 30% by weight have a distinctly increased purifying effect on waste water and 25 lead to optically almost clear or completely clear solutions.

According to a first embodiment of the present invention there is provided a precipitating or flocculating agent for waste water treatment, comprising double-layer hydroxides of the general composition (I)



30 wherein

M(II) is at least one divalent metal ion,

M(III) is at least one trivalent metal ion,

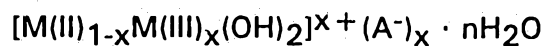
A is an equivalent of one or more mono- or polybasic acids,

x is between 0.01 and 0.5, and

35 n is between 0 and 20,

characterized in that the agent contains at least 30% by weight of hydrophilic solvents, and has solid particles with an average particle diameter of less than 2µm, and no particles with a particle diameter in excess of 10µm.

The present invention relates to a precipitant or flocculant for waste water treatment consisting of double-layer hydroxides of the general composition:



5 where

M(II) denotes at least one divalent metal ion,

M(III) denotes at least one trivalent metal ion,

A denotes an equivalent of one or more mono- or polybasic

acids,

10

x

assumes a value between 0.01 and 0.5, and

3
5
7
9
11
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15
17
19



n assumes a value between 0 and 20,
which is characterized in that it

- has a minimum content of hydrophilic solvents of 30% by weight so that

5 - the agglomeration of the primary particles to secondary particles which do not disintegrate in water is prevented to such an extent that their average particle diameter in an aqueous suspension is less than 2 μm and that no particles with a particle diameter in excess of 10 μm are present

10 and can be obtained either

(a) by feeding the salts used as initial materials for the preparation of this double-layer hydroxide in equivalent quantities in a solvent to a common reaction site and, after precipitation, using the precipitate, optionally after washing
15 with a solvent, in paste-like form without preliminary drying beyond a solids content of 70% by weight

or

(b) by forming the precipitate in situ in the waste water to be treated, taking the above measures into account.

20 The average particle diameter in the aqueous suspension is measured by a method known to the expert with the aid of a Coulter Counter of the company Coulter Electronic Ltd., England, making use of a 1% by weight aqueous sodium chloride solution as the electrolyte. The cited measurement conditions are explained in the manual of this instrument.

25 The process of preparing the precipitants or flocculants according to the invention implies that the initial materials are continuously fed to a reaction site so that none of the components is present in excess during the reaction. The continuous precipitation reaction is known for the production of composition hydroxides which are used, for example, as
30 acid binding agents as described in claim 4 of DE-OS 20 61 156. An alternative to this embodiment for combining the initial materials, viz. pumping the solutions of starting materials together through a Y tube, is described in EP-A-0 207 811 which relates to mixed metal hydroxides used as gel-forming agents for drilling fluids and the like.

35 In addition, within the purview of the present invention, it is essential that the ensemble of primary particles of the precipitant or flocculant according to the invention is kept stable to agglomeration prior to its use. According to the invention, this state is generally achieved by terminating the drying of the suspension present on



completion of precipitation and after acquiring a paste-like state with at least 30% by weight residual hydrophilic solvents has been reached. It may be assumed that the particularly fine primary particles obtained by the special precipitation process are kept in a dispersed state, 5 whereas, during drying, they form agglomerates of secondary particles which no longer disintegrate. This agglomeration effect has been described in the above-cited EP-A-0 207 811 where the addition of glycerol or other polyols is recommended with a view to avoiding agglomeration.

10 In the practical application of the process according to the invention, there is no need to add polyols which would result in a further contamination of the waste water to be treated. According to the invention, it is preferred not to isolate the double-layer hydroxide used at all and to carry out the precipitation directly in the wastewater to 15 be treated (Example 2). In this way, any loss of efficiency by ageing processes and agglomeration processes is avoided and a readily separable precipitate and a water-clear clean water phase are obtained.

However, one disadvantage of this procedure is that large quantities of fresh process water are required for preparing the 20 solutions of the initial material, which, technically, is expensive and leads to problems at the lastest when the precipitants and flocculants according to the invention and the process in which they are used are to be applied in areas where water is scarce. Accordingly, it is particularly preferred directly to produce the double-layer hydroxide in 25 the wastewater to be treated. For example, for this purpose, one dissolves the necessary quantities of initial materials of water-soluble salts with divalent and trivalent metal ions, preferably with magnesium and aluminium ions, in the minimum amount of water and introduces the resulting concentrated solution into the waste water to be treated 30 (Example 5). The solid water-soluble salts may also be directly dissolved in the waste water volume (Examples 3 and 4). In the case of alkaline waste water, which is what laundry waste water normally is, slight flocculation soon occurs, depending on the pH value. To complete flocculation, a pH value between 8 and 12 is adjusted, optionally with an 35 alkali hydroxide solution, for example a sodium hydroxide solution, pH values around 11 leading to a clearer clean water phase, albeit with an increased electrolyte content. At pH values around 9, slight clouding persists after separation of the precipitate, but the purified water's content of dissolved/dispersed constituents is lower than at higher pH



values.

The precipitates formed during the treatment may be separated by the conventional methods, such as sedimentation, flotation, filtration or centrifuging. The same also applies to a more extensive dehydration of
5 the sludge obtained, for which a chamber filter press, for example, may be used. The clean water obtained is completely clear to slightly clouded and has an electrolyte content of from about 6 to about 24 g/l.

Should this electrolyte content prove troublesome on account of the salting-up effect in the largely closed water circulation circuit, it may
10 be reduced by any of the methods known from the state of the art, e.g., by reverse osmosis or electrodialysis. The pH value, which is in the alkaline range because of the electrolyte concentration, is, in principle, favourable for re-use as a washing liquor.

It should be noted that membrane-based separation processes, such
15 as ultrafiltration, reverse osmosis or electrodialysis, cannot be directly used for purifying laundry waste waters because the membranes soon clog up if the waste water was not pretreated. This problem has been discussed in a paper by G.J. Van Gils, M. Pirbazari, S.-H. Kim and J. Shorr ("Treatment of Emulsified and Colloidal Industrial Waste water
20 Using a Combined Ultrafiltration-Carbon Adsorption Process", Proc. 39th Ind. Waste Conf., Purdue University 39, 269-280 (1985)). As a solution, the authors suggest pretreatment of the waste water with (expensive) active carbon or with the less effective (see Comparison Example 2) bentonite. The process according to the invention is an inexpensive and
25 effective alternative for the necessary pretreatment.

The invention is explained by the following by exemplary embodiments.

Used wash liquor (waste water from the wash cycle, "blue" washing) from an industrial-scale laundry was used for the Examples and Comparison
30 Examples. The indicated quantity of reagent was added to quantities of 500 ml of the wash liquor while stirring with a magnetic stirrer at room temperature, followed by stirring for 5 minutes. (In some tests, 2 ppm of a highly anionic flocculation aid (P_3 -Ferrocryl® 8723, a product of HENKEL KGaA; for further particulars, see Technische Information
35 [Information Pamphlet] K7-4/2)) were subsequently added, and stirring was continued for another 5 minutes at a reduced rate of rotation). Then filtering through a folded filter (pore size 5.8 μm according to DIN 12 448) was carried out and the filtration time for the first 200 ml was determined. In the filtrates, the pH value, the total electrolyte



content (drying at 110°C), and the relative degree of turbidity were determined. To measure turbidity, the absorption of light of the wavelength 520 nm was measured in a 1 cm cell in a Perkin-Elmer 124 double-beam spectrophotometer. The turbidity of the untreated wash liquor was set equal to 100% and the values of the treated samples were referred thereto.

The following abbreviations are used in the Examples and Comparison Examples:

	Filtration time for 200 ml:	FT
10	Turbidity, as % of the untreated wash liquor:	TR
	Appearance of the filtrate:	A
	Solids content of the filtrate, in g/l:	SC
	pH value:	pH

The figures in parentheses represent the values obtained upon addition of the flocculation aid Ferrocryl®.

Comparison Example 1

Untreated wash liquor

Result:	FT:	0.8 min
	TR:	100%
20	A:	dirty grey-brown
	SC:	7.7
	pH:	11.3

Comparison Example 2

Precipitation with 4 g active bentonite B

25 Result:	FT:	200 (170) min
	TR:	14.5 (23.1) %
	A:	yellowish cloudy (dto.)
	SC:	3.8 (3.8)
	pH:	11.2 (11.2)

30 Comparison Example 3

Precipitation with 4 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in accordance with FR-A-2 466 438

Result:	FT:	7.7 min (dto.)
	TR:	4.4 (5.8) %
35	A:	whitish cloudy (dto.)
	SC:	4.8 (4.9)
	pH:	5.1 (4.7)

Comparison Example 4

Precipitation with 4 g synthetic hydrotalcite powder (weight loss after

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drying for 4 h at 105°C: 3.2% by weight)

Result: FT: 13.1 min (13.5 min)

TR: 21 (31) %

A: dirty grey (dto.)

5 SC: 4.1 (3.8)

pH: 11.2 (11.2)

Example 1

A solution of 410 g magnesium nitrate hexahydrate and 300 g aluminium nitrate nonahydrate in 8,000 g fully deionized (DI) water (solution I) and a second solution of 448 g 50% by weight sodium hydroxide solution and 160 g sodium carbonate in 8,000 g DI water (solution II) are prepared. The two solutions are pumped together by means of hose pumps through the two arms of a Y-shaped tube into a glass beaker, the resulting hydrotalcite precipitate is filtered off under suction and then washed with DI water. 16 g (corresponding to 4 g hydrotalcite) of the paste-like product, which has a solids content of 25% by weight (as determined by drying of a sample at 100°C), are mixed by stirring into the wash liquor.

FT: 55.3 min (101 min)

20 TR: 7.9 (22.5) %

A: almost clear (dto.)

SC: 9.5 (6.25)

pH: 11.2 (11.3)

Example 2

25 The precipitant or flocculant, hydrotalcite, is precipitated directly into the wash liquor. To this end, quantities of 250 ml of reagent solutions I and II from Example 1 were pumped through the two arms of a Y-shaped tube into 500 ml wash liquor. The mixture obtained (1,000 ml) is divided; one half is filtered immediately and the other 30 half is filtered after mixing with Ferrocryl®.

FT: 1.5 min (1.6 min)

TR: 0.7 (0.7) %

A: water-clear (water-clear)

SC: 24 (23.5)

35 pH: 12.4 (12.3)

Example 3

The precipitant or flocculant is directly produced in the wash liquor: 1.73 g aluminium nitrate nonahydrate and 2.27 g magnesium nitrate hexahydrate are dissolved in 500 ml wash liquor and the pH value



is adjusted with sodium hydroxide to 9.

FT: 29.5 min (2.3 min)
TR: 3.6 (13) %
A: almost clear (dto.)
5 SC: 12.6 (8.0)
pH: 9.1 (9.4)

Example 4

A precipitant or flocculant is produced as described in Example 3, except that the magnesium nitrate is replaced by 2.27 g calcium nitrate
10 tetrahydrate.

FT: 6 min (3.2 min)
TR: 8.7 (7.9) %
A: almost clear (dto.)
SC: 10.4 (11.4)
15 pH: 9.1 (9.1)

Comparison Example 5

A new wash liquor was used for this Comparison Example.

FT: 1.1 min
TR: 100%
20 A: dirty grey-beige
SC: 10.3
pH: 12.4

Example 5

The precipitant or flocculant was produced in a new wash liquor
25 and, to this end, the initial materials were added in solution in a small volume of water: a solution of 0.65 g aluminium nitrate nonahydrate and 0.85 g magnesium nitrate hexahydrate in 5 ml fully deionized water was mixed with 500 ml of the wash liquor without stirring. After waiting for 5 minutes, the wash liquor was gently stirred and filtered.

30 FT: 45 min (42 min)
TR: 7.5 (10) %
A: water-clear (dto.)
SC: 12.2 (11.6)
pH: 11.4 (11.5)

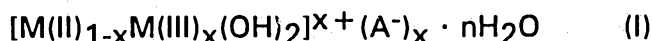
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The claims defining the invention are as follows:-

1. A precipitating or flocculating agent for waste water treatment, comprising double-layer hydroxides of the general composition (I)



5 wherein

M(II) is at least one divalent metal ion,

M(III) is at least one trivalent metal ion,

A is an equivalent of one or more mono- or polybasic acids,

x is between 0.01 and 0.5, and

10 n is between 0 and 20,

characterized in that the agent contains at least 30% by weight of hydrophilic solvents, and has solid particles with an average particle diameter of less than 2 μ m, and no particles with a particle diameter in excess of 10 μ m.

2. The agent according to Claim 1, characterized in that, in the
15 general formula (I), M(II) is magnesium or calcium and M(III) is aluminium or iron.

3. The agent according to Claim 1 or 2, characterized in that, in the general formula (I), A is carbonate, sulfate, (poly)phosphate, nitrate or chloride.

20 4. The agent according to Claim 3, characterized in that, in the general formula (I), A is carbonate.

5. The agent according to any one of Claims 1 to 4, characterized in that the agent is present in the form of an aqueous suspension or paste with a solids concentration of the range of 0.5 - 40% by weight.

25 6. A precipitating or flocculating agent for waste water treatment, substantially as hereinbefore described with reference to any one of Examples 1 to 5 but excluding the Comparative Examples.

7. A process for preparing a precipitating or flocculating agent according to any one of claims 1 to 6 comprising feeding salts used for
30 preparing the double-layer hydroxides in equal amounts in a solvent to a common reaction site, allowing a precipitate to form and removing the solvent until a solid substance concentration of at most 70% by weight has been reached.

8. A process according to claim 7, characterized in that the
35 precipitate is washed with a solvent before any solvent is removed.

9. The process according to Claim 7, characterized in that said solvent is water.

10. The process according to any one of Claims 7 to 9, characterized



in that water is added to the precipitate until an aqueous suspension or paste having a solids content of 0.5 to 40% by weight is obtained.

11. A process for preparing a precipitating or flocculating agent, substantially as hereinbefore described with reference to Example 1.

5 12. A precipitating or flocculating agent whenever prepared by the process according to any one of claims 7 to 11.

13. A waste water treatment process comprising adding a precipitating or flocculating agent according to any one of claims 1 to 6 or 12 to waste water to be treated and removing any solids from the waste water.

10 14. A waste water treatment process in which the precipitating or flocculating agent according to any one of claims 1 to 4 is formed in situ, characterized in that the salts used as the initial materials for the preparation of the double-layer hydroxides are fed in equivalent amounts in the form of solids or dissolved in water, directly into the waste water to be treated and
15 separating any solids produced.

15. The process according to Claim 14, characterized in that, after addition of the salts used as the initial materials to the waste water, the pH of the waste water is adjusted to the range of 8 to 13 by addition of alkali hydroxide.

20 16. The process according to Claim 15, characterized in that the pH is in the range of 9 to 12.

17. The process according to any one of Claims 7 to 11 or 14 to 16, characterized in that the solids content of the precipitating or flocculating agent is 0.2 to 3 times the solids content of the waste water.

25 18. The process according to any one of Claims 7 to 11 or 14 to 17, characterized in that, after precipitation and separation of the sludge, the clean water filtrate is further desalted by a membrane process before it is re-used as process water.

30 19. The process according to any one of Claims 7 to 11 or 14 to 18, characterized in the waste waters contain negatively charged contaminants.

20. The process according to any one of Claims 7 to 11 or 14 to 19, characterized in that the waste water is laundry waste.

21. A process for treating waste waters, substantially as hereinbefore described with reference to any one of Examples 2 to 5 but excluding the
35 Comparative Examples.

DATED this TWENTY FIFTH day of APRIL 1992

Henkel Kommanditgesellschaft auf Aktien

Patent Attorneys for the Applicant

SPRUSON & FERGUSON



INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 89/01324

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int. Cl. ⁵ C 02 F 1/52		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int. Cl. ⁵	C 02 F	
Documentation Searched other than Minimum Documentation to the extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ⁹	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	CHEMICAL ABSTRACTS, volume 91, 24 December 1979, COLUMBUS, OHIO, US, see page 305, abstract 216265s, & JP, A, 7993854 (KYOWA CHEMICAL IND. CO. LTD) 25 July 1979 cited in the application	1,6
A	CHIMIA, volume 24, March 1970, pages 99 - 108; R. Allmann: "Doppelschichtstrukturen mit brucitähnlichen Schichtionen" cited in the application	1,6
A	EP, A, 0056068 (HENKEL) 21 July 1982, see page 6, lines 15 - 33; page 9, see abstract	1,12
A	PROCEEDINGS OF THE 39TH INDUSTRIAL WASTE CONFERENCE, West Lafayette, Indiana, US pages 269 - 280; G.J. Van Gils: "Treatment of emulsified and colloidal industrial wastewater using a combined ultrafiltration-carbon adsorption process" cited in the application	11,12
	--	./.
⁹ Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
20 February 1990 (20.02.90)	22 March 1990 (22.03.90)	
International Searching Authority	Signature of Authorized Officer	
European Patent Office		

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	BE, A, 463541 (UNIFLOC REAGENTS LTD) 28 February 1947, see claims 1,2,8 -----	1,3,6

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

PCT/EP 89/01324
SA 32383

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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15/03/90

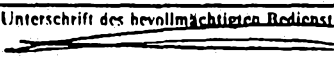
Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0056068	21-07-82	WO-A- 8202542 US-A- 4486314	05-08-82 04-12-84

BE-A-463541		None	

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen

PCT/EP 89/01324

I. KLASSIFIKATION DES ANMELDUNGSGEGENSTANDS (bei mehreren Klassifikationssymbolen sind alle anzugeben) ⁶		
Nach der Internationalen Patentklassifikation (IPC) oder nach der nationalen Klassifikation und der IPC		
Int.Kl. 5 C02F1/52		
II. RECHERCHIERTE SACHGEBIETE		
Recherchierter Mindestprüfstoff ⁷		
Klassifikationssystem	Klassifikationssymbole	
Int.Kl. 5	C02F	
Recherchierte nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Sachgebiete fallen ⁸		
III. EINSCHLAGIGE VERÖFFENTLICHUNGEN ⁹		
Art. ^o	Kennzeichnung der Veröffentlichung ¹¹ , soweit erforderlich unter Angabe der maßgeblichen Teile ¹²	Betr. Anspruch Nr. ¹³
A	CHEMICAL ABSTRACTS, vol. 91, 24 Dezember 1979, COLUMBUS, OHIO, US siehe Seite 305, Zusammenfassung 216265s, & JP, A, 7993854 (KYOWA CHEMICAL IND. CO. LTD) 25 Juli 1979 (in der Anmeldung erwähnt) ---	1, 6
A	CHIMIA vol. 24, März 1970, Seiten 99 - 108; R. Allmann: "Doppelschichtstrukturen mit brucitähnlichen Schichtionen" (in der Anmeldung erwähnt) ---	1, 6
A	EP,A,0056068 (HENKEL) 21 Juli 1982 siehe Seite 6, Zeilen 15 - 33; Seite 9 siehe Zusammenfassung ---	1, 12
-/-		
^o Besondere Kategorien von angegebenen Veröffentlichungen ¹⁰ : "A" Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist "E" älteres Dokument, das jedoch erst am oder nach dem internationalen Anmeldedatum veröffentlicht worden ist "L" Veröffentlichung, die geeignet ist, einen Prioritätsanspruch zweifelhaft erscheinen zu lassen, oder durch die das Veröffentlichungsdatum einer anderen im Recherchenbericht genannten Veröffentlichung belegt werden soll oder die aus einem anderen besonderen Grund angegeben ist (wie ausgeführt) "O" Veröffentlichung, die sich auf eine mündliche Offenbarung, eine Benutzung, eine Ausstellung oder andere Maßnahmen bezieht "P" Veröffentlichung, die vor dem internationalen Anmeldedatum, aber nach dem beanspruchten Prioritätsdatum veröffentlicht worden ist "T" Spätere Veröffentlichung, die nach dem internationalen Anmeldedatum oder dem Prioritätsdatum veröffentlicht worden ist und mit der Anmeldung nicht kollidiert, sondern nur zum Verständnis des der Erfindung zugrundeliegenden Prinzips oder der ihr zugrundeliegenden Theorie angegeben ist "X" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden "Y" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist "&" Veröffentlichung, die Mitglied derselben Patentfamilie ist		
IV. BESCHREIBUNG		
Datum des Abschlusses der internationalen Recherche	Abschließdatum des internationalen Recherchenberichts	
20. FEBRUAR 1990	22. 03. 90	
Internationale Recherchenbehörde	Unterschrift des bevollmächtigten Bediensteten	
EUROPAISCHES PATENTAMT	 T.K. WILDIS	

III. EINSCHLAGIGE VERÖFFENTLICHUNGEN (Fortsetzung von Blatt 2)

Art °	Kennzeichnung der Veröffentlichung, soweit erforderlich unter Angabe der maßgeblichen Teile	Betr. Anspruch Nr.
A	PROCEEDINGS OF THE 39TH INDUSTRIAL WASTE CONFERENCE, West Lafayette, Indiana, US Seiten 269 - 280; G.J. Van Gils: "Treatment of emulsified and colloidal industrial wastewater using a combined ultrafiltration-carbon adsorption process" (in der Anmeldung erwähnt) ---	11, 12
A	BE,A,463541 (UNIFLOC REAGENTS LTD) 28 Februar 1947 siehe Ansprüche 1, 2, 8 ---	1, 3, 6

**ANHANG ZUM INTERNATIONALEN RECHERCHENBERICHT
ÜBER DIE INTERNATIONALE PATENTANMELDUNG NR.**

PCT/EP 89/01324

SA 32383

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patendokumente angegeben.

Die Angaben über die Familienmitglieder entsprechen dem Stand der Datei des Europäischen Patentamts am
Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

15/03/90

Im Recherchenbericht angeführtes Patendokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie	Datum der Veröffentlichung
EP-A-0056068	21-07-82	WO-A- 8202542 US-A- 4486314	05-08-82 04-12-84
BE-A-463541		Keine	