(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 April 2005 (21.04.2005)

PCT

(10) International Publication Number
WO 2005/035449 A1

(51) International Patent Classification[7]: C02F 1/12, 1/52, 1/56, 1/68

(21) International Application Number: PCT/FI2004/000600

(22) International Filing Date: 11 October 2004 (11.10.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20031484 10 October 2003 (10.10.2003) FI

(71) Applicant *(for all designated States except US)*: **KEMIRA OYJ** [FI/FI]; Porkkalankatu 3, FI-00180 Helsinki (FI).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **JOKELA, Jukka** [FI/FI]; Tornipolku 12 A 7, FI-90100 Oulu (FI). **HIETAPELTO, Vesa** [FI/FI]; Angervotie 1 H 4, FI-90580 Oulu (FI).

(74) Agent: **BERGGREN OY AB**; P. O. Box 16 (Jaakonkatu 3 A), FI-00101 Helsinki (FI).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METAL COMPLEXED ORGANIC COAGULANT FOR PURIFICATION OF WASTE WATER

(57) Abstract: The invention relates to a coagulant in the form of a complex comprising an inorganic divalent or trivalent metal moiety and an organic polymer moiety, wherein the weight ratio of the organic polymer moiety to the inorganic moiety is in the range from 7:1 to 3:1. The invention also relates to a process for purification of municipal waste water.

WO 2005/035449 A1

Metal complexed organic coagulant for purification of waste water

The present invention relates to metal complexed organic coagulants for purification of municipal waste water, and to a process for purification of minicipal waste water.

GB 1 512 022 discloses a flocculating agent for water treatment comprising a concentrated aqueous solution of an inorganic flocculating agent and an organic cationic polymer. The inorganic flocculating agent comprises ferric sulphate, ferrous sulphate, aluminium chlorohydrate, aluminium sulphate or ferric sulphate, and the organic cationic polymer is for example a polyvinyl pyridine, a polyamide, a polyamine or a polyalkyleneimine. The flocculating agent is fed into a stream of an aqueous suspension of solid material causing formation and precipitation of a hydroxide corresponding to the inorganic flocculating agent. In the concentrated aqueous solution the amount of the inorganic flocculating agent is equal to a greater than the amount of the cationic polymer. The high amounts of the inorganic flocculating agent results in the formation of high amounts of sludge (iron or aluminium hydroxide) which is unfavourable in view of the further treament of the sludge.

GB 2 322 128 A discloses a coagulant for clarifying drinking water. This coagulant is formed by the reaction of an inorganic coagulant with a cationic polymer at elevated temperature, typically at a temperature in the range of 45-65°C. The inorganic coagulant is aluminium sulphate, ferric chloride, aluminium polyhydroxy-chlorosulphate or ferric sulphate, and the cationic polymer is obtained by polymerization of vinyl monomers such as diallyl dimethyl ammonium chloride. The amount of the polymer in relation to the inorganic coagulant is very small, and the amount of the polymer in the final product is also very small, typically 0.5% or 1% of the total weight of the final product. This coagulant is exclusively designed for the clarification of raw water (contaning minor amounts of organic substances, such as humic acids, and cations and anions) in drinking water treatment plants.

KR 2000059008 A discloses combined removal agents for coloring agents and COD in dyeing wastewater using decoloration and agglomeration. These combined removal agents are composed of a cationic polymer decolorant, a stabilizing agent and a coagulant, such as Fe(III) and alum. The polmer is made from dicyandiamide,

ammonium chloride and formalin. According to this document there is no reaction between the cationic polymer and the inorganic compounds.

GB 2 296 238 A discloses a composition for removal of dyes from textile industry effluents comprising a ferrous salt, a polyamine or a diallyldialkylammonium polymer (polydadmac) and a dicyandiamide-formaldehyde-ammonium chloride. These three components are added either as a blend or individually. This composition is claimed to provide a synergistic effect, and removing the final brown colour from the effluent.

WO 03/029151 A1 discloses a composition for use as a coagulation and flocculating agent in the purification of waste water. The diclosed composition consists of an aqueous solution of polyaluminium chloride as the main constituent, a magnesium or calcium compound and an organic polymer flocculating agent. The organic flocculating agent is a polyamine, a poly-diallyldimethyl-ammonium chloride, a polyethylenimine acetate or a polyethylenimine. The amont of the organic flocculating agent is preferably 20-25 parts by weight per 100 parts by weight of aluminium.

US 4 891 422 discloses inorganic-organic alloy polymer adduct compositions for purification of potable water, paper mill effluent or industrial waste water. The adduct composition is made from an inorganic polymer in reaction with a guanidine polymer or an organic alloy thereof with a polyamine, polyquaternized polymer, polyamide or polyamine-polyamide polymer. In the exemplified compositions the ratio of the polymer(s) to the metal(s) is typically very high, i.e. the amount of the metal is small in comparison to the amount of the polymer. The preferred metal component seems to be aluminium.

Most of the above discussed documents relate to the purification of drinking waters and specific industrial waste waters, such as dyed waste waters and waste waters from paper industry. On the contrary, the present invention is focussed on the purification of municipal waste waters. The major part of the organic loading from municipal waste water is organic matter having a specific particle size distribution. The soluble organic matter typically have a particle size of less than 0.1 μm whereas the colloids and suspended solids typically have a particle size of above 0.1 μm. Additionally, the municipal waste waters contain considarable amounts of dissolved nutrients, especially phosphorous.

The object of the present invention is to provide a coagulant for purification of municipal waste water, which coagulant provides a good purification efficiency, is easy to produce and produces a low amount of metal hydroxide sludge.

In a first aspect of the invention there is provided a coagulant in the form of a complex comprising an inorganic divalent or trivalent metal moiety and an organic polymer moiety, wherein the weight ratio of the organic polymer moiety to the inorganic moiety is in the range from about 7:1 to 3:1.

The metal complexed polymer coagulant of the invention is water soluble and cationic.

Said weight ratio of the organic polymer moiety to the inorganic moiety is preferably in the range from about 6:1 to 4:1, for example about 5:1.

Said organic polymer can be selected from the group consisting of

condensation products of alkylamines, polyalkyl amines, ammonia or a mixture thereof with polyfunctional aliphatic dihalides or halohydrins,
urea-formaldehyde condensation products,
melamineformaldehyde condensation products,
Mannich (co)polymers, and
polymers based on dicyandiamide or polymers from reaction of dicyandiamide and formaldehyde and optionally an ammonium salt and/or an alkylenepolyamine and/or urea.

Said organic polymer can also comprise the reaction or condensation products of two or more of the above polymers or condenstion products.

A preferred organic polymer comprises a polymer made from formaldehyde, dicyandiamide and ammonium chloride.

Said divalent or trivalent metal can be divalent or trivalent iron, trivalent aluminum or divalent copper. The metal is preferably trivalent iron.

A preferred metal complexed polymer coagulant of the invention is an Fe^{3+}-complexed dicyandiamide-formaldehyde-ammonium chloride polymer.

The metal complexed polymer coagulant is preferably in the form of an aqueous solution.

The metal complexed polymer coagulant of the invention can be obtained by reacting an organic polymer capable of forming a complex with a divalent or trivalent metal, and a source of a bivalent or trivalent metal in an aquous solution at a temperature of between 0°C and 45°C, preferably between 10°C and 30°C, and more preferably between 15°C and 25°C.

The source of the bivalent or trivalent metal can be a sulphate or chloride of said metal, for example ferric chloride, ferric sulphate, ferrous sulphate, aluminium sulphate (alum), aluminium chloride, hydroxyaluminium chloride, hydroxyaluminium sulphate, cupric sulphate or cupric chloride.

The above metal salts can be in solid form or in the form of an aqueous solution. The aqueous solution can be a concentrated solution of the metal salt.

The invention also relates to the use of the above defined metal complexed polymer coagulant for the purification of municipal waste water.

In a second aspect of the invention there is provided a process for purification of municipal waste water comprising the step of adding a coagulant to the municipal waste water, which coagulant is in the form of a complex comprising an inorganic divalent or trivalent metal moiety and an organic polymer moiety.

In the metal complexed polymer coagulant the weight ratio of the organic polymer moiety to the inorganic moiety is preferably in the range from about 7:1 to 3:1, more preferably from about 6:1 to 4:1, for example about 5:1. The metal complexed polymer coagulant is as defined above.

The metal complexed polymer coagulant can be added as an aqueous solution. The coagulant is preferably added in an amount per litre of 0.2 to 1.1 mg/NTU (Nephelometric Turbidity Unit) in the municipal waste water to be treated, calculated on the basis of dry substance of the coagulant. A more preferred amount is 0.6 to 1.0 mg/NTU.

The pH of normal municipal waste water is between 5 and 8. The metal complexed polymer coagulant of the invention can operate at pH values between 2 and 9.

The purification process of the invention can also include a biological treatment. Thus, in this embodiment the treatment with the coagulant is combined with a biological treatment. The treatment with the coagulant can a pre-treatment followed

by a biological treatment or a post-treatment preceded by a biological treatment. The biological treatment processes are well-known in the art.

Said biological treatment can be an aerobic or anaerobic process. A preferred aerobic biological treatment comprises treating the waste water in a moving bed biofilm reactor (MBBR).

The process of the present invention and the metal complexed polymer coagulant of the present invention remove very efficiently the organic substances (predominantly suspended solids and colloids) and phosphorous present in municipal waste waters.

In the production of the metal complexed polymer coagulant of the invention the manufacturing process is very simple and no heating is required. Furthermore the needed chemicals are inexpensive.

As the hydrolyis of the metal complexed polymer coagulant of the invention has been found to occur at a pH of above 7, the formation of metal hydroxides, such as iron hydroxides (i.e. amount of sludge) during the purification of the municipal waste water is expected to be low.

An advantage of the metal complexed polymer coagulant and the process of the invention is that due to the proportion of the polymer and metal in the complexed polymer coagulant, the amount of the metal hydroxide sludge will be very small and the precipitated sludge will have good dewatering ability facilitating the further treatment of the sludge, including for example dewatering and burning. Upon burning the sludge the ash content will be low. The sludge is also suitable for composting or as a land filling substance. Also the flocs are densely packed in the sludge whereby the volume of the sludge is small.

In the following the invention will be illustrated by means of examples and the enclosed drawing wherein

Fig. 1 shows results of sedimentation tests obtained by using an Fe^{3+}-complexed DCD polymer coagulant of the invention and a reference DCD polymer coagulant.

Example 1

An aqueous DCD polymer solution (prepared from formaldehyde, dicyandiamide and ammonium chloride) was used as starting material.

The Fe^{3+}-complexed DCD polymer coagulant is made by adding grinded $FeCl_3 \cdot 6H_2O$ (1 g) gradually into the DCD polymer solution (2g) and stirring the solution for 30 minutes as the iron dissolved at room temperature. A portion of the obtained coagulant (0.2 g) dissolved in 30ml distilled water was titrated by concentrated $NaHCO_3$ solution and the pH was monitored. A precipitate was formed at pH~6.8-7.0. From a pure Fe(III) solution iron hydroxide precipitates at pH<4. The complex formation between the trivalent iron and the DCD polymer prevents the precipitation of iron hydroxides below pH~7. As compared to the DCD polymer the Fe^{3+}-complexed DCD polymer of the invention has an increased cationic charge density in the molecule.

Example 2

Municipal waste water was subjected to sedimentation tests. Four different samples of the same waste water were treated with different doses of the Fe^{3+}-complexed DCD polymer (DCD+Fe) prepared in Example 1. The turbidity, total phosphorous (tot P) and chemical oxygen demand (COD) were measured. The results of the sedimentation tests are shown in Table 1 below.

Table 1

Test no	Coagulant	Composition			Polymer	Metal	T	pH	Turbidity	Tot P	COD
		Polymer % weight	Metal % weight	µl/l	mg/l	mg/l	°C		(NTU)	mg/l	mg/l
Initial							16	7.37	137	6.05	342
4	DCD+Fe	33.6	6.8	40	13.4	2.7			7.73	0.746	89.5
2	DCD+Fe	33.6	6.8	60	20.2	4.1	16	7.09	3.72	0.452	83.4
1	DCD+Fe	33.6	6.8	80	26.9	5.4	15	6.96	3.61	0.192	78.1
3	DCD+Fe	33.6	6.8	120	40.3	8.2	16	6.97	1.85	0.084	81

The above results show that the best turbidity was achieved with the highest dose (120 µl) of the coagulant, but also lower doses gave excellent results for e.g. turbidity and total phosphorous (tot P).

Example 3

Municipal waste water was subjected to sedimentation tests. In the first test the waste water sample was treated with pure DCD polymer, and in the second test the waste water sample was treated with the Fe^{3+}-complexed DCD polymer prepared in Example 1. By complexation it is possible to achieve much higher charge density in

the molecule. The results of the sedimentation tests (turbidity vs. dose) are shown in Fig. 1.

The test results show that the turbidity decreases noticeably, when the waste water is treated with the Fe^{3+}-complexed DCD polymer of the invention. This is due to the increased cationic charge density in the molecule. The reference DCD polymer was much less effective.

Example 4

Municipal waste water was taken from a pilot plant influent. The Fe^{3+} -complexed DCD polymer (DCD+Fe) prepared in Example 1 was tested at different doses.

The tests were carried out using a laboratory-scale flotation tester.

Clarified water was analysed for suspended solids (SS) using GF/C filter, turbidity, chemical oxygen demand (COD), and filtered COD (FCOD) (filtered through GF/C filter having nominal pore size of 1.2 μm). Dry solids (DC) and volatile solids (VS) were analysed from the sludge samples.

The analytical results from the tests are shown in Table 2 below.

Table 2

	Waste water	**DCD+Fe**		
		10 μL/L	**30 μL/L**	**50 μL/L**
SS (mg/L)	113	40	3	3
Turbidity (NTU)	62.5	23.1	1.16	0.29
COD (mg/L)	308	197	136	130
FCOD (mg/L)	157	140	132	129
Sludge DS (mg)		83	143	156
Sludge VS (mg)		64	110	119
pH	7.07			

The above test results show that the removal efficiencies were good in all cases.

Claims

1. A coagulant in the form of a complex comprising an inorganic divalent or trivalent metal moiety and an organic polymer moiety, wherein the weight ratio of the organic polymer moiety to the inorganic moiety is in the range from 7:1 to 3:1.

2. The coagulant according to claim 1 wherein the organic polymer is selected from the group consisting of

condensation products of alkylamines, polyalkyl amines, ammonia or a mixture thereof with polyfunctional aliphatic dihalides or halohydrins,
urea-formaldehyde condensation products,
melamineformaldehyde condensation products,
Mannich (co)polymers,
polymers based on dicyandiamide or polymers from reaction of dicyandiamide and formaldehyde and optionally an ammonium salt and/or an alkylenepolyamine and/or urea, and
reaction or condensation products of two or more of these polymers or condensation products.

3. The coagulant according to claim 1 or 2 wherein the organic polymer comprises a dicyandiamide-formaldehyde-ammonium chloride polymer.

4. The coagulant according to any of claim 1 to 3 wherein the divalent or trivalent metal is divalent or trivalent iron, trivalent aluminium or divalent copper.

5. The coagulant according to any of claims 1 to 4 wherein the divalent or trivalent metal comprises iron, preferably trivalent iron.

6. The coagulant according to any of claims 1 to 5 wherein the weight ratio of the organic polymer moiety to the inorganic moiety is in the range from 6:1 to 4:1.

7. The coagulant according to any of claims 1 to 6 wherein the coagulant is in the form of an aqueous solution.

8. The coagulant according to any of claims 1 to 7 wherein the coagulant is obtained by reacting an organic polymer capable of forming a complex with a divalent or trivalent metal, and a source of a bivalent or trivalent metal in an aquous solution at a temperature of between 0°C and 45°C, preferably between 10°C and 30°C.

9. Use of a coagulant of any of claims 1 to 8 for the purification of municipal waste waters.

10. A process for purification of municipal waste water comprising the step of adding a coagulant to the municipal waste water, which coagulant is in the form of a complex comprising an inorganic divalent or trivalent metal moiety and an organic polymer moiety.

11. The process according to claim 10 wherein in the coagulant the weight ratio of the organic polymer moiety to the inorganic moiety is in the range from 7:1 to 3:1, preferably from 6:1 to 4:1.

12. The process according to claim 10 or 11 wherein the coagulant is added as an aqueous solution in an amount per litre of 0.2 to 1.1 mg/NTU, preferably 0.6 to 1.0 mg/NTU in the municipalwaste water to be treated, calculated on the basis of dry content of the coagulant.

13. The process according to any of claims 10-12 wherein the treatment with the coagulant is combined with a biological treatment.

14. The process of claim 13 wherein the treatment with the coagulant is a pre-treatment followed by a biological treatment or a post-treatment preceded by a biological treatment.

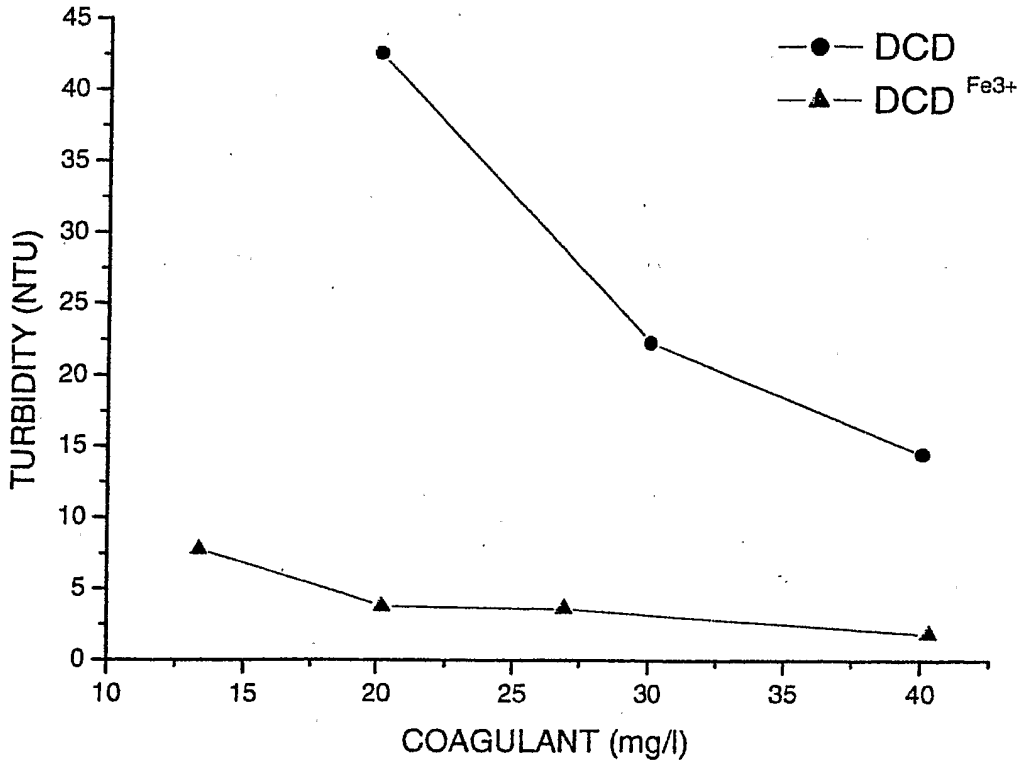
45
40
35
30
25
20
15
10
5
0
TURBIDITY (NTU)
10
15
20
25
30
35
40
COAGULANT (mg/l)
DCD
DCD Fe3+

Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/FI2004/000600

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C02F1/12 C02F1/52 C02F1/56 C02F1/68

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 424 702 A (KANEBO LTD) 11 February 1976 (1976-02-11)	1-8
A	page 3, lines 109-115 page 4, line 19; claim 1; table 12	9-14
A	GB 2 296 238 A (CHEMISOLV LTD) 26 June 1996 (1996-06-26) the whole document	1-14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"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 when the document is taken alone

"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

Date of the actual completion of the international search	Date of mailing of the international search report
14 January 2005	25/01/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Serra, R

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/FI2004/000600

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
GB 1424702	A	11-02-1976	JP	49105356 A	05-10-1974
			JP	885964 C	12-10-1977
			JP	49110146 A	19-10-1974
			JP	51048390 B	20-12-1976
			JP	1051414 C	26-06-1981
			JP	49002787 A	11-01-1974
			JP	55024939 B	02-07-1980
			JP	956255 C	31-05-1979
			JP	49023953 A	02-03-1974
			JP	53039707 B	23-10-1978
			DE	2321509 A1	15-11-1973
			FR	2182210 A1	07-12-1973
			IT	982835 B	21-10-1974
GB 2296238	A	26-06-1996	NONE		