



(11) **EP 1 741 774 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:  
**06.08.2008 Bulletin 2008/32**

(51) Int Cl.:  
**C11D 3/39<sup>(2006.01)</sup>** **C11D 1/66<sup>(2006.01)</sup>**  
**C11D 1/72<sup>(2006.01)</sup>**

(21) Application number: **06116118.8**

(22) Date of filing: **27.06.2006**

(54) **Machine dishwashing compositions and their use**

Maschinengeschirrspülmittel und deren Verwendung

Compositions pour lave-vaisselle automatique et leur utilisation

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR**

(30) Priority: **08.07.2005 EP 05076571**

(43) Date of publication of application:  
**10.01.2007 Bulletin 2007/02**

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**EP-A- 0 141 470** **WO-A-94/21775**  
**WO-A-95/06711** **US-A- 5 622 646**

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**Description**

**FIELD OF THE INVENTION**

5 **[0001]** This invention relates to detergent cleaning compositions especially adapted for use in automatic dishwashing machines.

**BACKGROUND OF THE INVENTION**

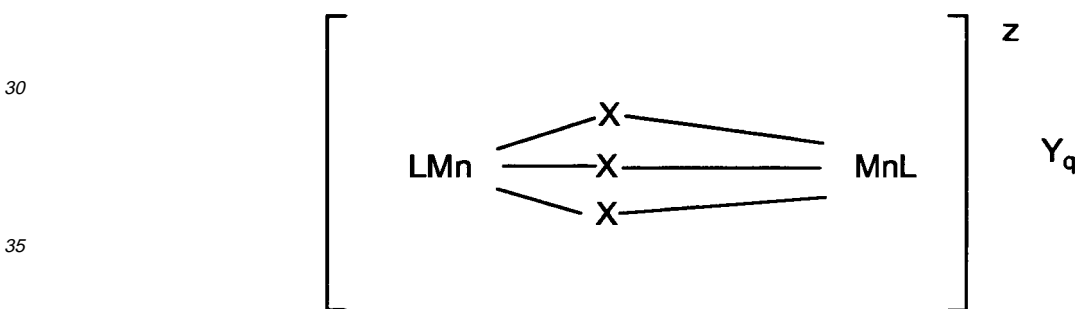
10 **[0002]** Automatic machine dishwashing products are nowadays, normally reduced phosphate or phosphate-free compositions which contain an oxygen bleach and enzymes, especially amylolytic and proteolytic enzymes, such as amylases and proteases. The oxygen bleach is typically sodium perborate or sodium percarbonate which advantageously may be used in conjunction with an organic activator or bleach precursor, e.g. N, N, N', N'-tetraacetylene diamine (TAED), which upon dissolution will react to form an organic peroxyacid, e.g. peracetic acid, as the bleaching species.

15 **[0003]** As is known from EP-A-0 530 870, the starch removal properties of an automatic machine dishwashing composition containing a peroxygen bleach can be improved by incorporation of a dinuclear manganese complex. However, products of this kind offer also contain nonionic surfactants. When the amount of nonionic surfactant is relatively high, particularly at or above 1% by weight of the composition, the manganese complex causes discolouration of the product.

20 **[0004]** We have now found that this problem can be overcome by special selection of the type of nonionic surfactant.

**DEFINITION OF THE INVENTION**

25 **[0005]** A first aspect of the present invention now provides an automatic machine dishwashing composition comprising at least 1%, preferably at least 2% by weight of nonionic surfactant, a peroxygen bleach compound and a dinuclear manganese-complex having the general formula:



40 wherein Mn is manganese which can individually be in the III or IV oxidation state; each x represents a coordinating or bridging species selected from the group consisting of H<sub>2</sub>O, O<sub>2</sub><sup>2-</sup>, O<sup>2-</sup>, OH<sup>-</sup>, HO<sub>2</sub><sup>-</sup>, SH<sup>-</sup>, S<sup>2-</sup>, >SO, Cl<sup>-</sup>, N<sup>3-</sup>, SCN<sup>-</sup>, RCOO<sup>-</sup>, NH<sub>2</sub><sup>-</sup> and NR<sub>3</sub>, with R being H, alkyl or aryl, (optionally substituted); L is a ligand which is an organic molecule containing a number of nitrogen atoms which coordinates via all or some of its nitrogen atoms to the manganese centres; z denotes the charge of the complex and is an integer which can be positive or negative; Y is a monovalent or multivalent counterion, leading to charge neutrality, which is dependent upon the charge z of the complex; and q = <sup>z</sup>[charge Y];

45 wherein at least 50% by weight of the nonionic surfactant is selected from:

- (a) at least one nonionic surfactant having a melting point greater than 35°C, preferably greater than 40°C.

50 **[0006]** A second aspect of the present invention provides use of one or more nonionic surfactant components (a) as defined in the first aspect of the present invention for reducing discolouration in a composition comprising a peroxygen bleach compound and a dinuclear manganese complex as defined in the first aspect of the present invention.

**[0007]** Preferably, the machine dishwashing composition is a mildly alkaline product having a solution pH below 12, e.g. from 8-12, preferably from 9-11.

55 **[0008]** The solution pH as meant here is the pH as determined from a solution of 3g/l of the compositions in distilled water.

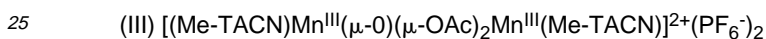
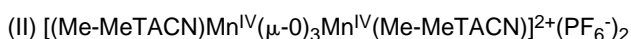
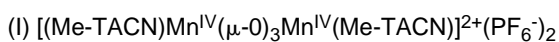
**DETAILED DESCRIPTION OF THE INVENTION**The Dinuclear Manganese Complex

5 **[0009]** Preferred manganese-complexes are those wherein x is either  $\text{CH}_3\text{COO}^-$  or  $\text{O}^{2-}$  or mixtures thereof, most preferably wherein the manganese is in the IV oxidation state and x is  $\text{O}^{2-}$ . Preferred ligands are those which coordinate via three nitrogen atoms to one of the manganese centres, preferably being of a macrocyclic nature. Particularly preferred ligands are:

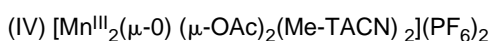
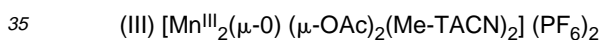
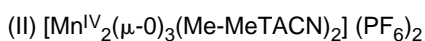
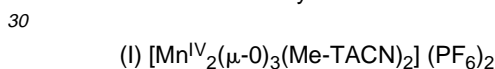
- 10 (1) 1,4,7-trimethyl-1,4,7-triazacyclononane, (Me-TACN); and  
 (2) 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, (Me-Me TACN).

15 **[0010]** The type of counter-ion Y for charge neutrality is not critical for the activity of the complex and can be selected from, for example, any of the following counter-ions: chloride; sulphate; nitrate; methylsulphate; surfactant anions, such as the long-chain alkylsulphates, alkylsulphonates, alkylbenzenesulphonates, tosylate, trifluoromethylsulphonate, perchlorate ( $\text{ClO}_4^-$ ),  $\text{BPh}_4^-$ , and  $\text{PF}_6^-$  though some counter-ions are more preferred than others for reasons of product property and safety.

20 **[0011]** Consequently, the preferred manganese complexes useable in the present invention are:



which hereinafter may also be abbreviated as:

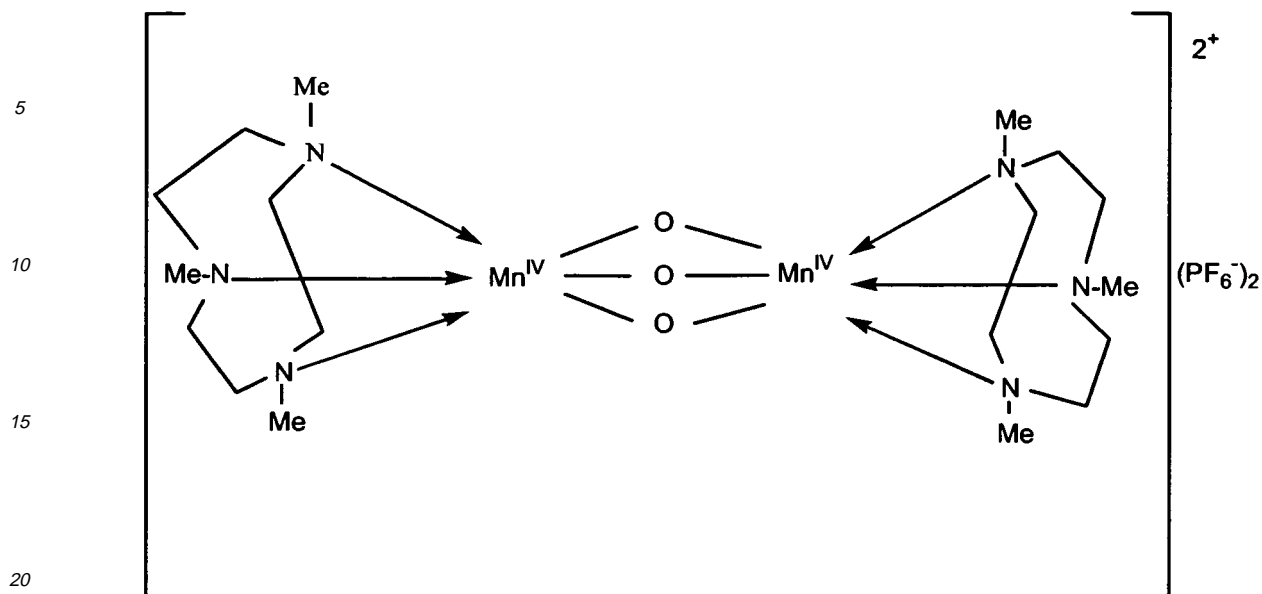


40 **[0012]** The structure of I is given below:

45

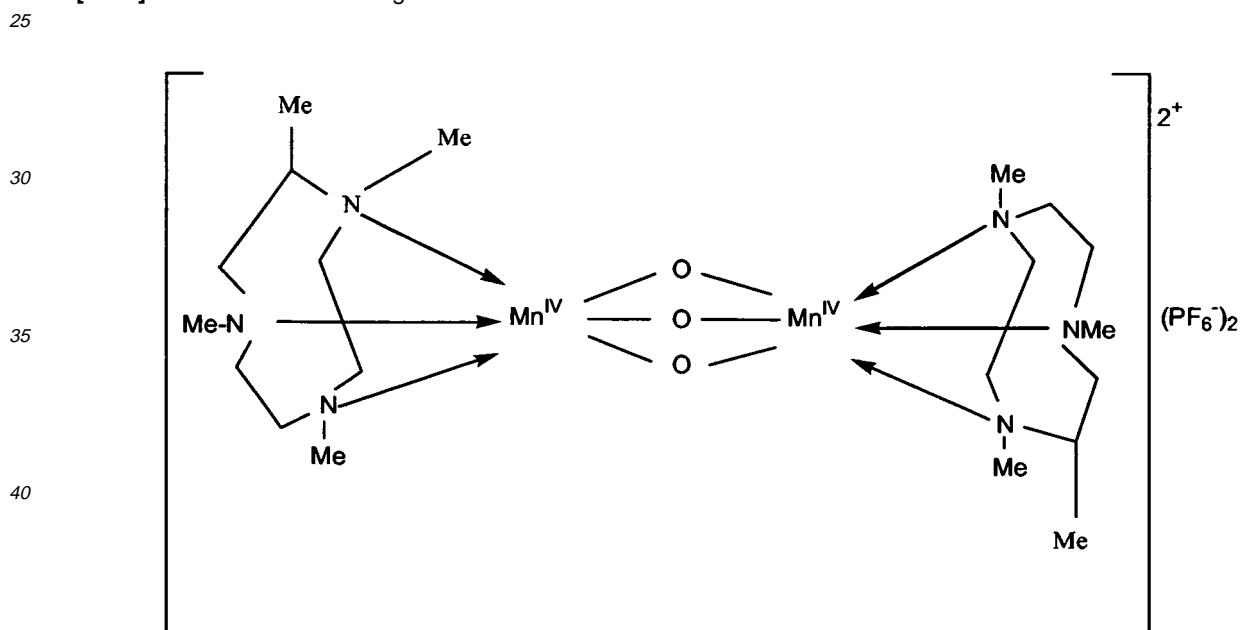
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abbreviated as  $[Mn^{IV}_2(\mu-O)_3(Me-TACN)_2] (PF_6^-)_2$ .

**[0013]** The structure of II is given below:



abbreviated as  $[Mn^{IV}_2(\mu-O)_3(Me-MeTACN)_2] (PF_6^-)_2$

**[0014]** It is of note that the manganese complexes are also disclosed in EP-A-0458397 and EP-A-0458398 as unusually effective bleach and oxidation catalysts. In the further description of this invention they will also be simply referred to as the "catalyst".

**[0015]** These complexes are effective additives for starch removal in mechanical dishwashing compositions, even in the absence of amylolytic enzymes. Whereas amylolytic enzymes are not normally compatible with strong oxidizing and bleaching agents, a bleach system comprising a peroxide compound and the manganese complex bleach catalyst does not seem to attack amylolytic enzymes, so that both systems can be used together to provide a still further improvement of starch removal.

The Nonionic Surfactant

**[0016]** The compositions of the invention must contain at least 1%, preferably at least 2% by weight of nonionic surfactant. At least 50%, preferably at least 65%, optionally up to 90% or up to 100% by weight of the total nonionic surfactant must be selected from

(a) at least one nonionic surfactant having a melting point greater than 35°C, preferably greater than 40°C;

**[0017]** Preferably, nonionic surfactants of group (a) are present in the composition of the invention. Preferred nonionic surfactants of group (a) include hydroxyalkyl glycoether surfactants having a melting point above 35°C, preferably above 40°C. A preferred class of such materials has from 6 to 20, preferably from 8 to 14 carbon atoms in the alkyl chain thereof and from 15 to 50, preferably from 20 to 40 glycol ether units. One such material is Dehypon 3697 GRAM, ex Cognis. Other suitable nonionic surfactants of this group are high melting point polyalkoxylated alcohols, optionally with the -OH group endcapped such as with an alkyl group and typically having an average of 10 to 20 alkyl groups and more than 30 alkylene oxide groups, eg ethylene oxide and/or propylene oxide groups.

**[0018]** Optionally, one or more other nonionics may be present in the amounts indicated by the foregoing. These may include any alkoxylated nonionic surface-active agent wherein the alkoxy moiety is selected from the group consisting of ethylene oxide, propylene oxide and mixtures thereof, is preferably used to improve the detergency and to suppress excessive foaming due to some protein soil.

**[0019]** Examples of suitable nonionic surfactants for use in the invention are the low- to non-foaming ethoxylated straightchain alcohols of the Plurafac® RA and LF series, supplied by the BASF, including Plurafac SLF 18B45; of the Lutensol® LF series, supplied by the BASF; of the Tritons DF series, supplied by the Rohm & Hass Company, and of the Synperonic® LF and NCA series, supplied by the ICI, Uniqema company.

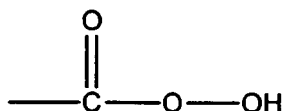
The Peroxygen Bleach Compound

**[0020]** The peroxygen compound bleaches which can be utilized in the present invention include hydrogen peroxide, hydrogen peroxide-liberating compounds, hydrogen peroxide-generating compounds, as well as the organic and inorganic peroxyacids and watersoluble salts thereof, and mixtures thereof.

**[0021]** The total amount of peroxygen bleach compound(s) is preferably from 5% to 25%, more preferably from 10% to 20% by weight of the composition.

**[0022]** Hydrogen peroxide sources are well known in the art. They include the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as the alkali metal perborates, percarbonates, perphosphates and persulphates. Mixtures of two or more of such compounds may also be suitable. Particularly preferred is sodium percarbonate. However, sodium perborate, eg in the form sodium perborate monohydrate may also be used. Sodium perborate monohydrate is preferred to tetrahydrate because of its better storage stability while also dissolving very quickly in aqueous solutions. These bleaching agents may be utilized alone or in conjunction with a peroxyacid bleach precursor, such as TAED or any other bleach precursors known in the art, so long as it does not affect the starch-removing properties of the catalyst.

**[0023]** The organic peroxyacids usable in this invention are those compounds known in the art having normally one or more peroxycarboxyl groups:



in their molecular structure, e.g. 1,12 - diperoxydodecanedioic acid (DPDA) and phthaloylamido peroxycaproic acid (PAP). An inorganic peroxyacid salt usable herein is, for example, potassium monopersulphate.

Detergency Builder

**[0024]** Compositions according to the present invention may also normally contain a detergency and water-softening builder. Builder materials may be selected from 1) calcium sequestrant materials, 2) precipitating materials, 3) calcium ion-exchange materials and 4) mixtures thereof.

**[0025]** Examples of calcium sequestrant builder materials include alkali metal polyphosphates, such as sodium tripolyphosphate; nitrilotriacetic acid, dipicolinic acid, chelidamic acid and their water-soluble salts; the alkali metal salts of ether

polycarboxylates, such as carboxymethyloxy succinic acid, oxydisuccinic acid, mellitic acid; ethylene diamine tetraacetic acid; benzene polycarboxylic acids; citric acid; and polyacetal carboxylates as disclosed in US Patents 4,144,226 and 4,146,495.

**[0026]** Examples of precipitating builder materials include sodium orthophosphate, sodium carbonate and sodium carbonate/calcite.

**[0027]** Examples of calcium ion-exchange builder materials include the various types of water-insoluble crystalline or amorphous aluminosilicates, of which zeolites are the best-known representatives. Other useful materials are, for example, layered silicates, such as SKS®-6 ex Hoechst.

**[0028]** The compositions of the invention may contain any one of the organic or inorganic builder materials, such as sodium or potassium tripolyphosphate, sodium or potassium pyrophosphate, sodium or potassium orthophosphate, sodium carbonate or sodium carbonate/calcite mixtures, the sodium salt of nitrilotriacetic acid, sodium citrate, carboxymethyl malonate, carboxymethyloxy succinate and the water-insoluble crystalline or amorphous aluminosilicate builder materials, or mixtures thereof, although phosphates are less preferred.

**[0029]** Preferred compositions are, however, essentially free of phosphates and will contain, for example, alkali metal citrate, alkali carbonate, alkali metal carbonate/calcite, aluminosilicates (zeolites) or mixtures thereof as preferred builder materials. In all of these, the alkali metal is sodium or potassium, preferably sodium. The citrates are especially preferred.

**[0030]** Other suitable non-phosphate builders which may be used alone or in combination with any one or more other builders include methyl glycine diacetic acid (MGDA), eg sold as Trilon M, ex BASF, imino disuccinate (IDS) eg sold as Baypure CS, ex Lanxess and dipicolinic acid (DPA), eg available from Raschig. The alkali metal salts (eg sodium salts) of these are also useable.

**[0031]** It should be noted that some of the foregoing inorganic detergency builders may have a dual role, eg the carbonates may also act as buffering agents (see below).

**[0032]** The total amount of detergency builder, for example comprising any one or more of any of the foregoing may for example be from 10% to 80%, preferably from 30% to 60% by weight of the total composition.

**[0033]** An optional but highly desirable additive ingredient with multi-functional characteristics, particularly in non-phosphate compositions is from 1% to 10%, preferably about 5% by weight of a polymeric material having a molecular weight of from 1,000 to 2,000,000 and which can be a homo- or co-polymer of acrylic acid, maleic acid, or salt or anhydride thereof, vinyl pyrrolidone methyl- or ethyl-, vinyl ethers and other polymerizable vinyl monomers. Preferred examples of such polymeric materials are polyacrylic acid or polyacrylate; polymaleic acid/acrylic acid copolymer; 70:30 acrylic acid/hydroxyethyl maleate copolymer; 1:1 styrene/maleic acid copolymer; isobutylene/maleic acid and diisobutylene/maleic acid copolymers; methyl- and ethyl-vinylether/maleic acid copolymers; ethylene/maleic acid copolymer; polyvinyl pyrrolidone; and vinyl pyrrolidone/maleic acid copolymer. These polymers are believed to function as co-builders, although under certain conditions they may also function as main builders.

### Buffering Agent

**[0034]** Buffering agents may be used in compositions according to the present invention in order to adjust and to maintain the alkalinity and pH at the desired level. These are for example, the alkali metal carbonates and bicarbonates, sometimes also borates, and silicates. If used, sodium silicates preferably have  $\text{Na}_2\text{O}:\text{SiO}_2$  ratios of from about 2:1 to 1:4. Another possible buffering agent is sodium disilicate having  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio of about 1:1.8 to 1:2.5.

### Enzymes

**[0035]** Though not essential, the cleaning compositions in which the catalyst is used according to the invention may, as desired, contain an amylolytic enzyme, though conceivably a much smaller amount will now be sufficient.

**[0036]** Reduction of the level of once an essential ingredient to even the possibility of omitting such an expensive enzyme ingredient, thereby resulting in improved performance, is one of the major advantages of the present invention, not only in terms technical benefit but also in terms of economy.

**[0037]** The amylolytic enzymes for use in the present invention can be those derived from bacteria or fungi. Preferred amylolytic enzymes are those prepared and described in British Patent Specification No. 1 296 839, cultivated from the strains of *Bacillus licheniformis* NCIB 8061, NCIB 8059, ATCC 6334, ATCC 6598, ATCC 11 945, ATCC 8480 and ATCC 9945. Examples of such amylolytic enzymes are amylolytic enzymes produced and distributed under the trade name of Sp-95® or Termamyl® by Novo Industri A/S, Copenhagen, Denmark, as well as Termamyl and Duramyl, ex Novozymes and Properase and Purastar ex Genecor. These amylolytic enzymes are generally presented as granules and may have enzyme activities of from about 2 to 10 Maltose units/milligram. Enzyme granules containing only minor proportions, e.g. less than 30%, particularly not more than 10% by weight of chloride to substantially nil, are preferably used in the compositions of the invention.

**[0038]** The amylolytic activity can be determined by the method as described by P. Bernfeld in "Method of Enzymology"

Volume 1 (1955), page 149.

**[0039]** The composition in which the catalyst is used according to the invention preferably also contains a proteolytic enzyme.

**[0040]** Examples of suitable proteolytic enzymes are the subtilisins which are obtained from particular strains of **B. subtilis** and **B.licheniformis**, such as the commercially available subtilisins Maxatase® supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase®, supplied by Novo Industri A/S, Copenhagen, Denmark.

**[0041]** Particularly suitable is a protease obtained from a strain of Bacillus having maximum activity throughout the pH range of 8-12, being commercially available from Novo Industri A/S under the registered trade names of Esperase® and Savinase®. The preparation of these and analogous enzymes is described in British Patent No. 1 243 784. Another suitable protease useful herein is a fairly recent commercial product sold by Novo Industry A/S under the trade name "Durazym®" as described in WO-A-89/06279. These enzymes are generally presented as granules, e.g. marumes, prills, T-granulates etc., and may have enzyme activities of from about 500 to 1700 glycine units/milligram. The proteolytic activity can be determined by the method as described by M.L. Anson in "Journal of General Physiology". Vol. 22 (1938), page 79 (one Anson Unit/g = 733 Glycine Units/milligram).

**[0042]** Enzyme granules containing only minor proportions, e.g. less than 30%, particularly not more than 10% by weight of chloride to substantially nil, are preferably used in the composition of the invention.

**[0043]** If used, these enzymes can each be present in a weight percentage amounts of from 0.2 to 5% by weight, such that, for amylolytic enzymes, the final composition will have amylolytic activity of from  $10^2$  to  $10^6$  Maltose units/kg, and, for proteolytic enzymes, the final composition will have proteolytic enzyme activity of from about  $10^6$  to  $10^9$  Glycine Units/kg.

#### Optional Other Ingredients

**[0044]** The compositions according to the present invention may further contain any of the following additional ingredients. Stabilizing and anti-scaling agents, crystal-growth inhibitors and threshold agents. Examples of suitable stabilizing and anti-scaling compounds are those belonging to the class of phosphonates sold under the trade name "Dequest®", such as ethylene diamine tetra-(methylene phosphonate), diethylene triamine penta-(methylene phosphonate) and ethylene hydroxyl diphosphonate. Another suitable class of anti-scaling agents are the low molecular weight polyacrylates, polymaleates and mixtures thereof or the copolymers thereof, having molecular weights of up to about 6000. A further suitable class of anti-scaling agents are polypeptides.

**[0045]** Benzotriazole (BTA) may be used as a silver protection agent. Zinc salts may be used as glass corrosion inhibitors and sulphonated polymers (eg Alcosperse 240) may be used as anti-scaling polymers.

**[0046]** Clays such as hectorites and montmorillonites, may be included in the composition of the invention. These assist in reduction of spot formation on glassware, and may be present at from 0.5 to 10% by weight, preferably from 0.5 to 7% by weight. Particularly preferred is the addition of Laponite® clay at about 0.5 to 5% by weight, which is a synthetic hectorite. "Dequest" and "Laponite" are Trade Marks owned by, respectively, Monsanto and Laporte Industries.

**[0047]** Finally, the addition of a filler may be required to complete the composition, though, in compacted powdered compositions it should preferably be avoided. A preferred filler is sodium sulphate.

#### Typical Formulations

**[0048]** A typical composition according to the present invention may include from 0 to 80%, preferably from 5 to 60% by weight of a detergency and water-softening builder, from 0 to 80%, preferably 5 to 75% by weight of a buffering agent, from 1 to 40%, preferably from 2 to 20% by weight of a peroxygen compound bleach, and optionally an enzyme and fillers and may further comprise a dinuclear manganese complex as defined above, in an amount corresponding to an Mn-content of from 0.0001 to about 1.0% by weight, preferably from 0.0005 to 0.5% by weight.

**[0049]** The invention will now be further illustrated by the following Examples.

#### Product Form

**[0050]** Compositions of the present invention may be in any suitable physical form, for example powdered and/or granular compositions or tablets. Tablets may be unitary or comprise two or more layers having differing compositions from each other, the tablet as a whole having the total constituents making-up the composition according to the present invention. Some or all of the dinuclear manganese complex may be in the same or in a different layer from a layer containing some or all of the nonionic surfactant, eg some or all of the nonionic surfactant component(s) (a) - (c) and/or any other non-ionic surfactant. Cavity tablets, eg with a spherical or ball component set into the cavity are also preferred. Again the manganese complex may in this way optionally be at least partially segregated from some or all of any or all of the nonionic surfactant component(s), whether components (a) - (c) or any other nonionic surfactant.

**EXAMPLES**

**[0051]** Two tablets were made, respectively designated "Comparative Example A" and "Example 1", the latter being in accordance with the present invention. In each case, the respective components were incorporated in powdered or granular form and dry-mixed before being compacted to form tablets.

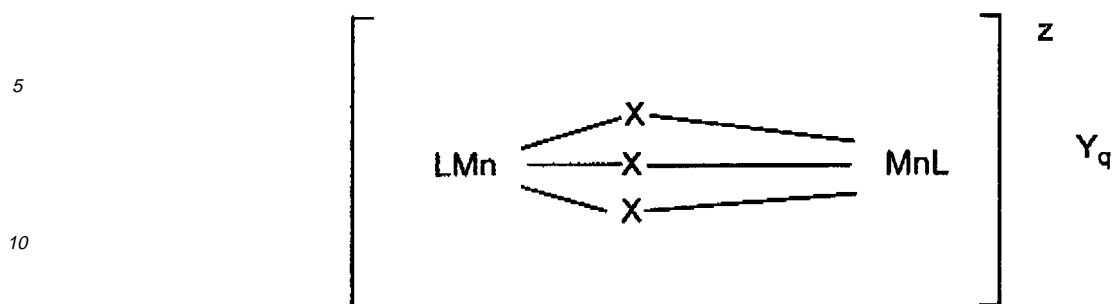
Table 1

|  | Comparative example A | Example 1 |
|--|-----------------------|-----------|
| Tri Na Citrate   | 31.51                 | 31.51     |
| Na Carbonate   | 20.13                 | 20.13     |
| Na Sulphate  | 7.00                  | 7.00      |
| Na-silicate  | 9.96                  | 9.96      |
| Sodium acrylic/maleic copolymer                                      | 3.90                  | 3.90      |
| Polyacrylate granule   | 1.17                  | 1.17      |
| Styrene/Maleic anhydride copolymer                                   | 0.23                  | 0.23      |
| EP/PO nonionic*  | 4.00                  | 1.26      |
| Hydroxy Alkyl Polyglycoether nonionic**                              |                       | 2.74      |
| Na Percarbonate  | 13.66                 | 13.66     |
| Manganese catalyst cogranule+  | 1.22                  | 1.22      |
| Enzyme blend   | 2.68                  | 2.68      |
| Perfume  | 0.14                  | 0.14      |
| Dye solution   | 0.42                  | 0.42      |
| PEG  | 3.11                  | 3.11      |
| Glycerol   | 0.86                  | 0.86      |
| 100.00   | 100.00                | Total     |
| * m.pt. < 20°C   |                       |           |
| ** m.pt. approx 60°C   |                       |           |
| + complex of formula (I):(PF <sub>6</sub> ) <sub>2</sub> counter ion |                       |           |

**[0052]** After storage at 20°C and at 65% RH, for 2 weeks in a polypropylene bag, the tablets of Comparative Example A showed noticeable formation of brown spots whereas those of Example 1 showed substantially no discolouration.

**Claims**

1. An automatic machine dishwashing composition comprising at least 1%, preferably at least 2% by weight of nonionic surfactant, a peroxygen bleach compound and a dinuclear manganese-complex having the general formula:



15 wherein Mn is manganese which can individually be in the III or IV oxidation state; each x represents a coordinating or bridging species selected from the group consisting of  $\text{H}_2\text{O}$ ,  $\text{O}_2^{2-}$ ,  $\text{O}^{2-}$ ,  $\text{OH}^-$ ,  $\text{HO}_2^-$ ,  $\text{SH}^-$ ,  $\text{S}^{2-}$ ,  $>\text{SO}$ ,  $\text{Cl}^-$ ,  $\text{N}^{3-}$ ,  $\text{SCN}^-$ ,  $\text{RCOO}^-$ ,  $\text{NH}_2^-$  and  $\text{NR}_3$ , with R being H, alkyl or aryl, (optionally substituted); L is a ligand which is an organic molecule containing a number of nitrogen atoms which coordinates via all or some of its nitrogen atoms to the manganese centres; z denotes the charge of the complex and is an integer which can be positive or negative; Y is a monovalent or multivalent counter-ion, leading to charge neutrality, which is dependent upon the charge z of the complex; and  $q = z/[\text{charge Y}]$ :

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wherein at least 50% by weight of the nonionic surfactant is selected from:

25 (a) at least one nonionic surfactant having a melting point greater than  $35^\circ\text{C}$ , preferably greater than  $40^\circ\text{C}$ .

2. A composition according to claim 1, wherein the non-ionic surfactant having a melting point greater than  $35^\circ\text{C}$  is selected from one or more hydroxyalkyl polyglycoethers and optionally endcapped polyalkoxylated alcohols having at least 30 alkyleneoxy groups and mixtures thereof.

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3. A composition according to any preceding claim, comprising a nonionic surfactant in the form of a granule having pores with a number average pore size less than  $5\mu\text{m}$ , the pores containing the nonionic surfactant; and mixtures thereof, wherein the granule is formed of one or more alkali metal carbonates, bicarbonates, sulphates and mixtures thereof.

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4. A composition according to any preceding claim, wherein the peroxygen bleach compound comprises an alkali metal percarbonate.

5. A composition according to any preceding claim further comprising a bleach precursor or activator.

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6. A composition according to any preceding claim, the composition being substantially free of phosphate material.

7. A composition according to any preceding claim, further comprising a citrate detergency builder.

8. A composition according to any preceding claim, wherein the dinuclear manganese complex comprises a ligand selected from

45

- (1) 1,4,7-trimethyl-1,4,7-triazacyclononane, (Me-TACN); and  
 (2) 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, (Me-Me TACN).
- 50

and mixtures thereof.

9. A tablet comprising composition according to any preceding claim.

10. Use of one or more nonionic surfactant components (a):

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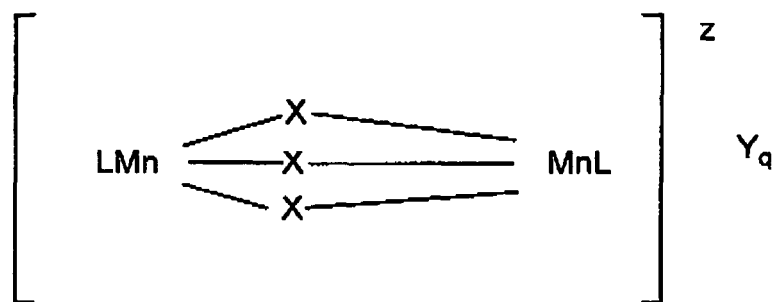
(a) at least one nonionic surfactant having a melting point greater than  $35^\circ\text{C}$ , preferably greater than  $40^\circ\text{C}$ ;

for reducing discolouration in a composition comprising a peroxygen bleach compound and a dinuclear manganese complex having the general formula:

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wherein Mn is manganese which can individually be in the III or IV oxidation state; each x represents a coordinating or bridging species selected from the group consisting of H<sub>2</sub>O, O<sub>2</sub><sup>2-</sup>, O<sup>2-</sup>, OH<sup>-</sup>, HO<sub>2</sub><sup>-</sup>, SH<sup>-</sup>, S<sup>2-</sup>, >SO, Cl<sup>-</sup>, N<sup>3-</sup>, SCN<sup>-</sup>, RCOO<sup>-</sup>, NH<sub>2</sub><sup>-</sup> and NR<sub>3</sub>, with R being H, alkyl or aryl, (optionally substituted); L is a ligand which is an organic molecule containing a number of nitrogen atoms which coordinates via all or some of its nitrogen atoms to the manganese centres; z denotes the charge of the complex and is an integer which can be positive or negative; Y is a monovalent or multivalent counter-ion, leading to charge neutrality, which is dependent upon the charge z of the complex; and q = z/[charge Y].

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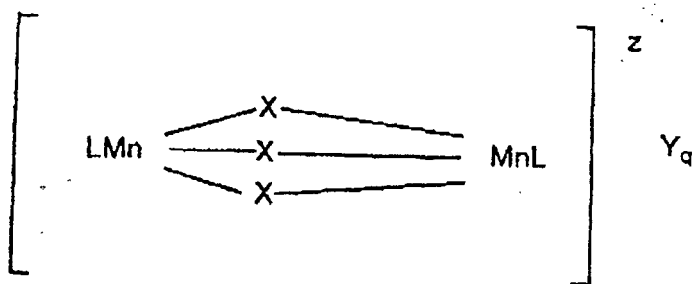
### Patentansprüche

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1. Maschinengeschirrspülmittel, umfassend wenigstens 1 Gew.-%, vorzugsweise wenigstens 2 Gew.-% nicht-ionisches Tensid, eine Peroxygen-Bleichmittelverbindung und einen zweikernigen Mangankomplex mit der allgemeinen Formel:

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worin Mn Mangan ist, welches individuell in der III- oder IV-Oxidationsstufe sein kann; jedes x eine koordinierende oder brückenbildende Species darstellt, ausgewählt aus der Gruppe, bestehend aus H<sub>2</sub>O, O<sub>2</sub><sup>2-</sup>, O<sup>2-</sup>, OH<sup>-</sup>, HO<sub>2</sub><sup>-</sup>, SH<sup>-</sup>, S<sup>2-</sup>, >SO, Cl<sup>-</sup>, N<sup>3-</sup>, SCN<sup>-</sup>, RCOO<sup>-</sup>, NH<sub>2</sub><sup>-</sup> und NR<sub>3</sub>, wobei R H, Alkyl oder Aryl (gegebenenfalls substituiert) ist; L ein Ligand ist, welcher ein organisches Molekül ist, das eine Reihe von Stickstoffatomen enthält, das über alle oder einige seiner Stickstoffatome an die Manganzentren koordiniert; z die Ladung des Komplexes bezeichnet und eine ganze Zahl ist, die positiv oder negativ sein kann; Y ein monovalentes oder multivalentes Gegenion ist, das zur Ladungsneutralität führt, das von der Ladung z des Komplexes abhängig ist, und q = z/[Ladung Y];

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wobei wenigstens 50 Gew.-% des nicht-ionischen Tensids ausgewählt sind aus:

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- (a) wenigstens einem nicht-ionischen Tensid mit einem Schmelzpunkt von höher als 35 °C, vorzugsweise höher als 40 °C.

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2. Mittel nach Anspruch 1, wobei das nicht-ionische Tensid, das einen Schmelzpunkt von höher als 35 °C hat, ausgewählt ist aus einem oder mehreren Hydroxyalkylpolyglykolethern und gegebenenfalls endverkappten polyalkoxylierten Alkoholen, die wenigstens 30 Alkylenoxygruppen haben, und Gemischen davon.
- 5 3. Mittel nach einem vorangehenden Anspruch, umfassend ein nicht-ionisches Tensid in der Form eines Körnchens, das Poren mit einer zahlenmittleren Porengröße von weniger als 5 µm hat, wobei die Poren das nicht-ionische Tensid enthalten; und Gemische davon, wobei das Körnchen aus einem oder mehreren Alkalicarbonaten, -bicarbonaten, -sulfaten und Gemischen davon gebildet ist.
- 10 4. Mittel nach einem vorangehenden Anspruch, wobei die Peroxygen-Bleichmittelverbindung ein Alkalimetallpercarbonat umfasst.
5. Mittel nach einem vorangehenden Anspruch, das außerdem einen Bleichmittelvorläufer oder -aktivator umfasst.
- 15 6. Mittel nach einem vorangehenden Anspruch, wobei das Mittel im Wesentlichen frei von Phosphatmaterial ist.
7. Mittel nach einem vorangehenden Anspruch, das außerdem einen Citrat-Builder umfasst.
8. Mittel nach einem vorangehenden Anspruch, wobei der zweikernige Mangankomplex einen Liganden, ausgewählt aus

- (1) 1,4,7-Trimethyl-1,4,7-triazacyclononan, (Me-TACN), und  
 (2) 1,2,4,7-Tetramethyl-1,4,7-triazacyclononan, (Me-Me-TACN)

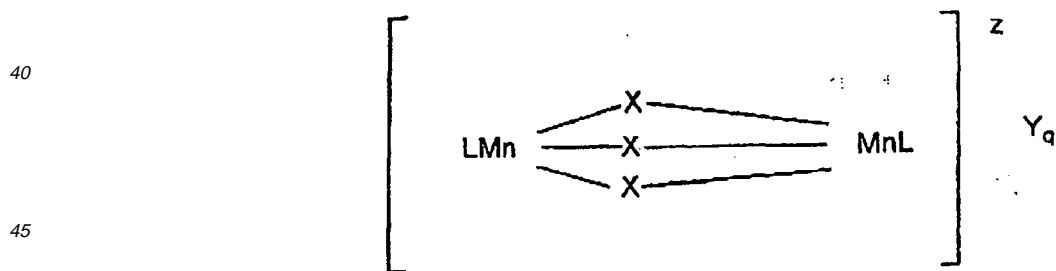
25 und Gemischen davon, umfasst.

9. Tablette, umfassend das Mittel nach einem vorangehenden Anspruch.

30 10. Verwendung eines oder mehrerer nicht-ionischer Tensidkomponente(n) (a)

(a) wenigstens eines nicht-ionischen Tensids, das einen Schmelzpunkt von höher als 35 °C, vorzugsweise höher als 40 °C, hat,

35 zur Verringerung einer Verfärbung in einem Mittel, das eine Peroxygen-Bleichmittelverbindung und einen zweikernigen Mangankomplex mit der allgemeinen Formel:

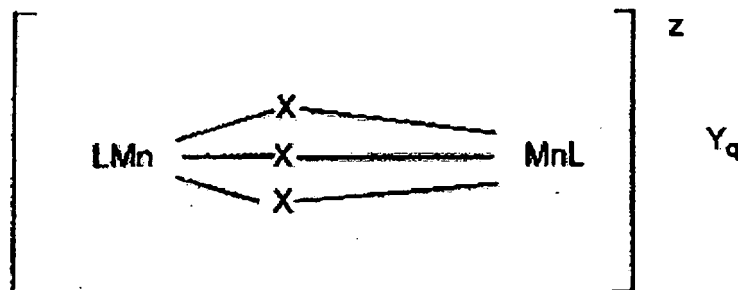


50 umfasst, worin Mn Mangan ist, welches individuell in der III- oder IV-Oxidationsstufe sein kann; jedes x eine koordinierende oder brückenbildende Species darstellt, ausgewählt aus der Gruppe, bestehend aus H<sub>2</sub>O, O<sub>2</sub><sup>2-</sup>, O<sup>2-</sup>, OH<sup>-</sup>, HO<sub>2</sub><sup>-</sup>, SH<sup>-</sup>, S<sup>2-</sup>, >SO, Cl<sup>-</sup>, N<sup>3-</sup>, SCN<sup>-</sup>, RCOO<sup>-</sup>, NH<sub>2</sub><sup>-</sup> und NR<sub>3</sub>, wobei R H, Alkyl oder Aryl (gegebenenfalls substituiert) ist; L ein Ligand ist, welcher ein organisches Molekül ist, das eine Reihe von Stickstoffatomen enthält, das über alle oder einige seiner Stickstoffatome an die Manganzentren koordiniert; z die Ladung des Komplexes bezeichnet und eine ganze Zahl ist, die positiv oder negativ sein kann; Y ein monovalentes oder multivalentes Gegenion ist, das zur Ladungsneutralität führt, das von der Ladung z des Komplexes abhängig ist, und q = z/[Ladung Y].

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## Revendications

1. Composition pour lave-vaisselle automatique comprenant au moins 1 %, de préférence au moins 2 % en poids d'un tensioactif non ionique, un composé de blanchiment au peroxygène et un complexe binucléaire de manganèse ayant la formule générale :



dans laquelle Mn est le manganèse qui peut être individuellement à l'état d'oxydation III ou IV ; chaque x représente une espèce de coordination ou de pontage choisie dans le groupe constitué par H<sub>2</sub>O, O<sub>2</sub><sup>2-</sup>, O<sup>2-</sup>-OH<sup>-</sup>, HO<sub>2</sub><sup>-</sup>, SH<sup>-</sup>, S<sup>2-</sup>, >SO, Cl<sup>-</sup>, N<sup>3-</sup>, SCN<sup>-</sup>, RCOO<sup>-</sup>, NH<sub>2</sub><sup>-</sup> et NR<sub>3</sub>, R étant H, alkyle ou aryle (éventuellement substitué) ; L est un ligand qui est une molécule organique contenant un certain nombre d'atomes d'azote qui se coordonne par l'intermédiaire de tous ou de quelques-uns de ses atomes d'azote aux centres de manganèse ; z désigne la charge du complexe et est un entier qui peut être positif ou négatif ; Y est un contre-ion monovalent ou multivalent, induisant la neutralité de la charge, qui dépend de la charge z du complexe ; et q = z/[charge Y] ; dans laquelle au moins 50 % en poids du tensioactif non ionique est choisi parmi :

- (a) au moins un tensioactif non ionique ayant un point de fusion supérieur à 35 °C, de préférence supérieur à 40 °C.
2. Composition selon la revendication 1, dans laquelle le tensioactif non ionique ayant un point de fusion supérieur à 35 °C est choisi parmi un ou plusieurs éthers polyglycols hydroxyalkylés et alcools polyalcoylés éventuellement aux extrémités coiffées ayant au moins 30 groupes alkylèneoxy et des mélanges de ceux-ci.
  3. Composition selon l'une quelconque des revendications précédentes, comprenant un tensioactif non ionique dans la forme d'un granulé ayant des pores avec une dimension de pore moyenne en nombre inférieure à 5 μm, les pores contenant le tensioactif non ionique ; et des mélanges de celui-ci, dans laquelle le granulé est formé d'un ou plusieurs carbonates, bicarbonates, sulfates de métaux alcalins et de mélanges de ceux-ci.
  4. Composition selon l'une quelconque des revendications précédentes, dans laquelle le composé de blanchiment au peroxygène comprend un percarbonate de métal alcalin.
  5. Composition selon l'une quelconque des revendications précédentes, comprenant en outre un précurseur ou activateur de blanchiment.
  6. Composition selon l'une quelconque des revendications précédentes, la composition étant sensiblement dépourvue de matériau phosphaté.
  7. Composition selon l'une quelconque des revendications précédentes, comprenant en outre un adjuvant de détergence au citrate.
  8. Composition selon l'une quelconque des revendications précédentes, dans laquelle le complexe binucléaire de manganèse comprend un ligand choisi parmi :

- (1) le 1,4,7-triméthyl-1,4,7-triazacyclononane, (Me-TACN) ; et
- (2) le 1,2,4,7-tétraméthyl-1,4,7-triazacyclononane, (Me-Me TACN) ;

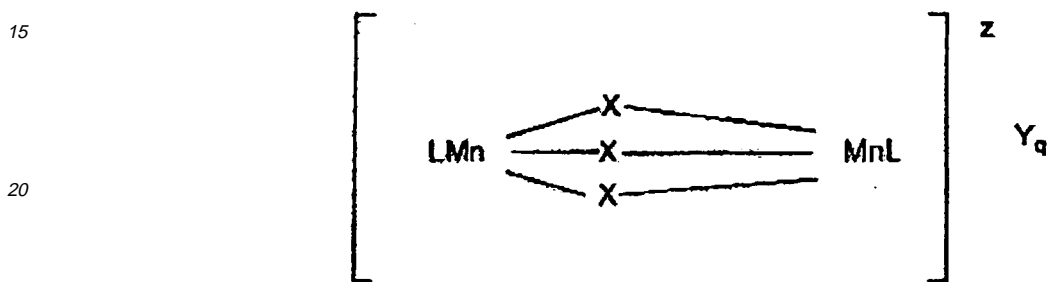
et des mélanges de ceux-ci.

9. Tablette comprenant une composition selon l'une quelconque des revendications précédentes.

5 10. Utilisation d'un ou plusieurs composants tensioactifs non ioniques (a) :

(a) au moins un tensioactif non ionique ayant un point de fusion supérieur à 35 °C, de préférence supérieur à 40°C ;

10 pour réduire l'altération de la couleur dans une composition comprenant un composé de blanchiment au peroxygène et un complexe binucléaire de manganèse ayant la formule générale :



25 dans laquelle Mn est le manganèse qui peut être individuellement à l'état d'oxydation III ou IV ; chaque x représente une espèce de coordination ou de pontage choisie dans le groupe constitué par H<sub>2</sub>O, O<sub>2</sub><sup>2-</sup>, O<sup>2-</sup>, OH<sup>-</sup>, HO<sub>2</sub><sup>-</sup>, SH<sup>-</sup>, S<sup>2-</sup>, >SO, Cl<sup>-</sup>, N<sup>3-</sup>, SCN<sup>-</sup>, RCOO<sup>-</sup>, NH<sub>2</sub><sup>-</sup> et NR<sub>3</sub>, R étant H, alkyle ou aryle (éventuellement substitué) ; L est un ligand qui est une molécule organique contenant un certain nombre d'atomes d'azote qui se coordonne par l'intermédiaire de tous ou de quelques-uns de ses atomes d'azote aux centres de manganèse ; z désigne la charge du complexe et est un entier qui peut être positif ou négatif ; Y est un contre-ion monovalent ou multivalent, induisant la neutralité de la charge, qui dépend de la charge z du complexe ; et q = z/[charge Y].

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**REFERENCES CITED IN THE DESCRIPTION**

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