AUSTRALIAN PATENT OFFICE SEC 113

AUSTRALIA SPRUSON & FERGUSON

PATENTS ACT 1990

PATENT REQUEST: STANDARD PATENT

I/We, the Applicant(s)/Nominated Person(s) specified below, request I/We be granted a patent for the invention disclosed in the accompanying standard complete specification.

[70,71] Applicant(s)/Nominated Person(s):

Ciba Specialty Chemicals Holding Inc
~~Ciba-Geigy AG, incorporated in Switzerland~~, of Klybeckstrasse 141, ~~4002 Basle~~, SWITZERLAND
CH-4057 Basel

[54] Invention Title:

Inhibition of Dye Migration

[72] Inventor(s):

Claude Eckhardt, Dieter Reinehr and Georges Metzger

[74] Address for service in Australia:

Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia (Code **SF**)

Details of Basic Application(s):

[31] Appl'n No(s):	**[33] Country:**	**[32] Application Date:**
9425296.2	GB	15 December 1994

DATED this EIGHTH day of DECEMBER 1995

Ciba-Geigy AG

By:

Registered Patent Attorney

IRN: 319006

INSTR CODE: 52760

S 062033 141295

SPRUSON & FERGUSON

Australia

Patents Act 1990

Notice Of Entitlement

I, John David O'Connor, of 31 Market Street, Sydney, New South Wales, 2000, Australia, Patent Attorney for the Applicant/Nominated Person in respect of an application entitled:

Inhibition of Dye Migration

state the following:-

The Applicant/Nominated Person has entitlement from the actual inventors as follows:-

The Applicant/Nominated Person is the assignee of the actual inventors.

The Applicant/Nominated Person is the applicant of the basic application listed on the Patent Request.

The basic application listed on the Patent Request is the first application made in a Convention Country in respect of the invention.

Dated 23 November 1995

John David O'Connor

IRN: 319006

INSTR CODE: 52760

[N:\LIBT]23200:ZLA

AU9540462

(12) PATENT ABRIDGMENT (11) Document No. AU-B-40462/95
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 699655

(54) Title
INHIBITION OF DYE MIGRATION

International Patent Classification(s)

(51)[6]	C07D 213/74	C07C 233/56	C07C 251/16	C07C 251/24
	C07C 251/70	C07D 213/53	C07D 255/02	C07D 255/04
	C07D 257/10	C07D 487/18	C07D 487/22	D06P 001/62
	D06P 001/642			

(21) Application No. : **40462/95** (22) Application Date : **14.12.95**

(30) Priority Data

(31) Number	(32) Date	(33) Country
9425296	**15.12.94**	**GB UNITED KINGDOM**

(43) Publication Date : **20.06.96**

(44) Publication Date of Accepted Application : **10.12.98**

(71) Applicant(s)
CIBA SPECIALTY CHEMICALS HOLDING INC.

(72) Inventor(s)
CLAUDE ECKHARDT; DIETER REINEHR; GEORGES METZGER

(74) Attorney or Agent
SPRUSON & FERGUSON , GPO Box 3898, SYDNEY NSW 2001

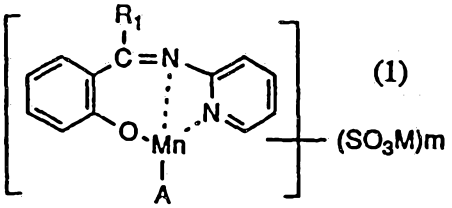
(56) Prior Art Documents
AU 64817/94

(57) **Please note: The compounds in claim 1 are claimed per se in claim 29.**

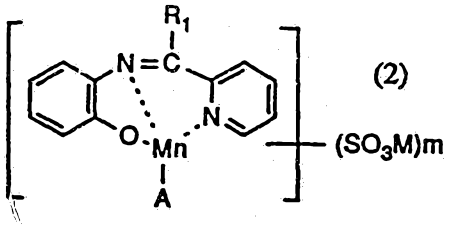
The present invention relates to a process for inhibiting the re-absorption of migrating dyes in the wash liquor.

Claim

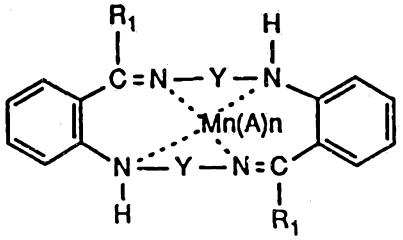
1. A process for inhibiting the re-absorption of migrating dyes in the wash liquor, comprising introducing into a wash liquor containing a peroxide-containing detergent, from 0.5 to 150 mg, per litre of wash liquor, of one or more compounds having the formula (1), (2), (3), (4), (5), (6), (7), (8), (9), (10), (11), (12), (13) or (14):



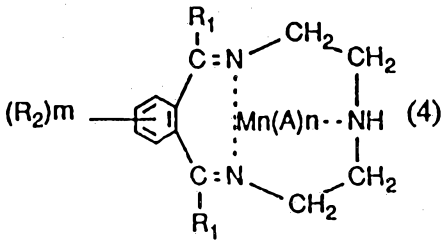
(1)



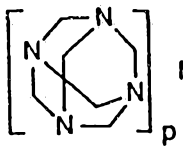
(2)


R1
H
C=N—Y—N
Mn(A)n
N—Y—N=C
H
R1

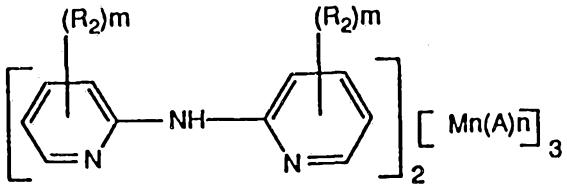
(3)


R1
CH2
CH2
C=N
(R2)m
Mn(A)n··NH
C=N
CH2
CH2
R1

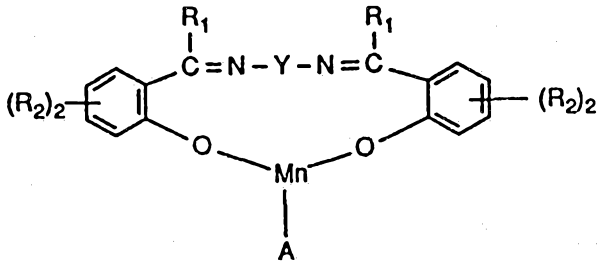
(4)


N
N
N
N
p

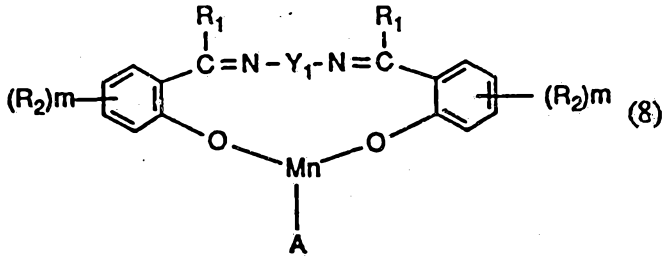
Mn(A)n (5)


(R2)m
(R2)m
NH
N
N
2
Mn(A)n
3

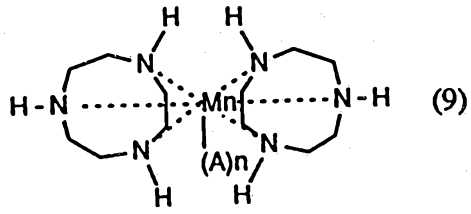
(6)


R1
R1
C=N-Y-N=C
(R2)2
(R2)2
O
O
Mn
A

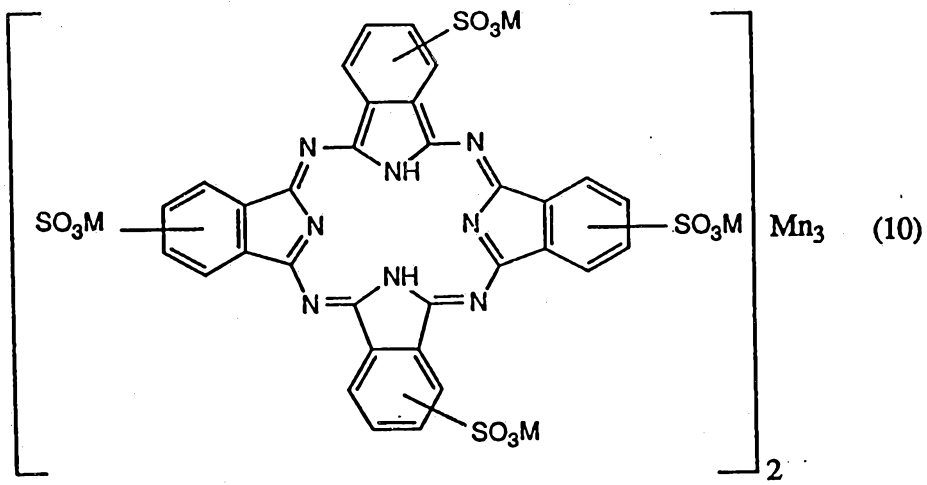
(7)


R1
R1
C=N-Y1-N=C
(R2)m
(R2)m
O
O
Mn
A

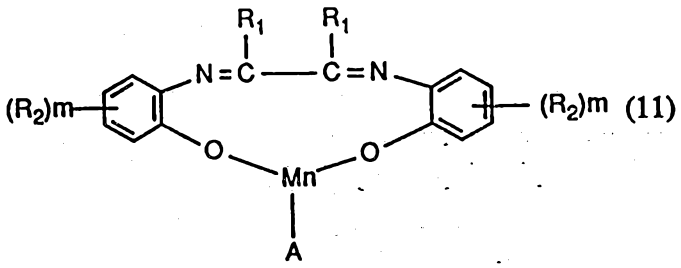
(8)



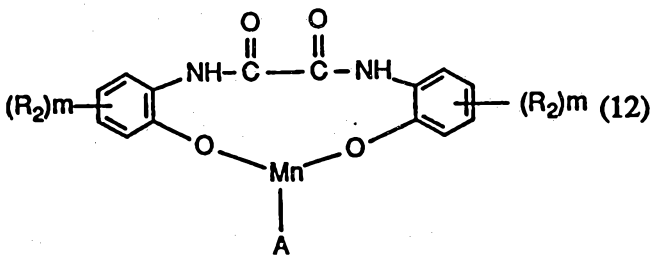
(9)



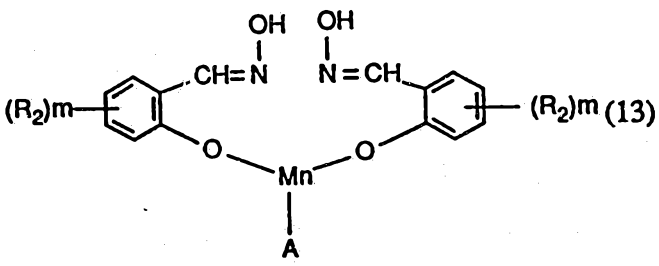
(10)



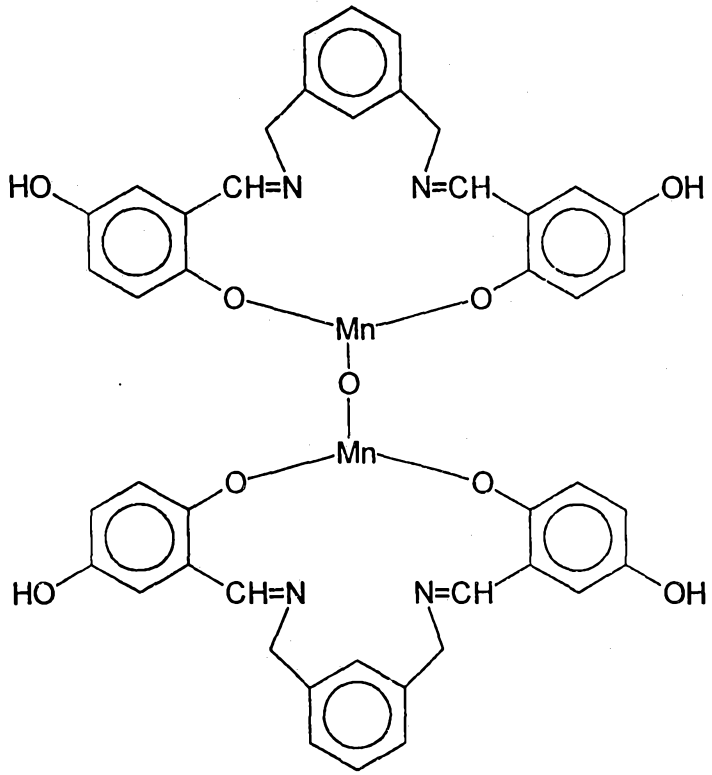
(11)



(12)



(13)



(14)

in which R_1 is hydrogen or optionally substituted alkyl, cycloalkyl or aryl; R_2 is hydrogen, optionally substituted alkyl, optionally substituted alkoxy, halogen, cyano, N(optionally substituted alkyl)$_2$, $N^{\oplus}$(optionally substituted alkyl)$_3$ or a water-solubilising group; Y is optionally substituted alkylene, cyclohexylene or arylene; Y_1 is C_2-C_4 alkylene, optionally interrupted by a nitrogen atom, a 1,4-methanocyclohexylene residue or a phenylene residue optionally substituted by a group SO_3M; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; n is 2 or 3; m is 0 or 1; p is 1 or 2; and A is an anion; with the proviso that R_2 must not be hydrogen, unsubstituted alkyl or SO_3M if either m is 1 and Y_1, is optionally substituted alkylene or cycloalkylene.

S & F Ref: 319006

AUSTRALIA

PATENTS ACT 1990

COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL



Name and Address of Applicant: Ciba Specialty Chemicals Holding Inc
~~Ciba-Geigy AG~~
Klybeckstrasse 141
~~4002 Basle~~ CH-4057
SWITZERLAND

Actual Inventor(s): Claude Eckhardt, Dieter Reinehr and Georges Metzger

Address for Service: Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Invention Title: Inhibition of Dye Migration

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

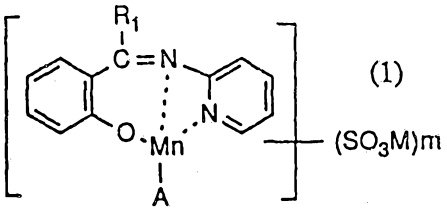
Inhibition of dye migration

The present invention relates to a process for inhibiting the re-absorption of migrating dyes in the wash liquor.

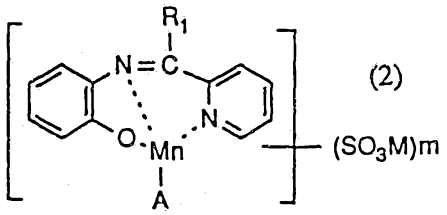
It is well known that various metal compounds, e.g. manganese complexes, are useful in detergents as catalysts for peroxides.

It has now been found that certain other manganese complexes exert a pronounced bleaching effect on dirt or dyes in the wash bath. Moreover, these manganese complexes do not exhaust at all on to cotton, polyamide or polyester fibres so that the complexes cannot lead to fibre discolouration problems.

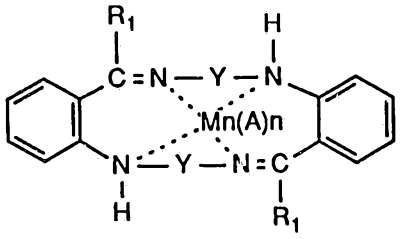
Accordingly, the present invention provides a process for inhibiting the re-absorption of migrating dyes in the wash liquor, comprising introducing into a wash liquor containing a peroxide-containing detergent, from 0.5 to 150, preferably from 1.5 to 75, especially from 7.5 to 40 mg, per litre of wash liquor, of one or more compounds having the formula (1), (2), (3), (4), (5), (6), (7), (8), (9), (10), (11), (12), (13) or (14):



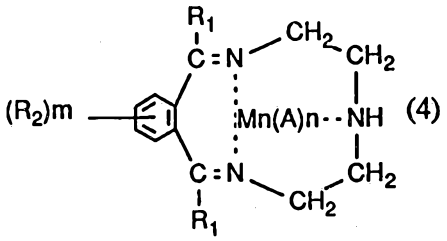
(1)



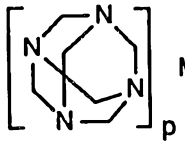
(2)


R1
H
C=N—Y—N
Mn(A)n
N—Y—N=C
H
R1

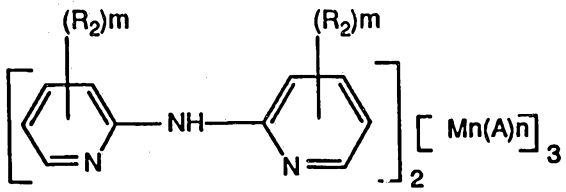
(3)


R1
C=N
CH2
CH2
(R2)m
Mn(A)n
NH
C=N
CH2
R1
CH2

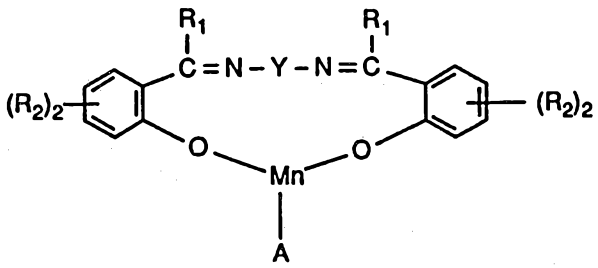
(4)


N
N
N
N
p

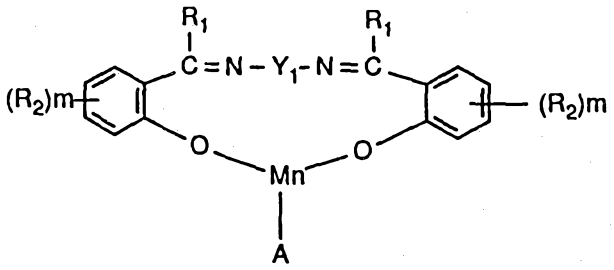
Mn(A)n (5)


(R2)m
(R2)m
NH
N
N
2
Mn(A)n
3

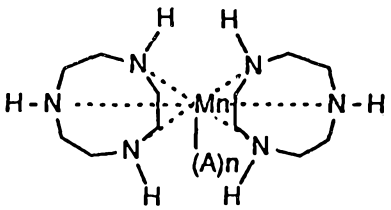
(6)


R1
R1
C=N-Y-N=C
(R2)2
(R2)2
O
O
Mn
A

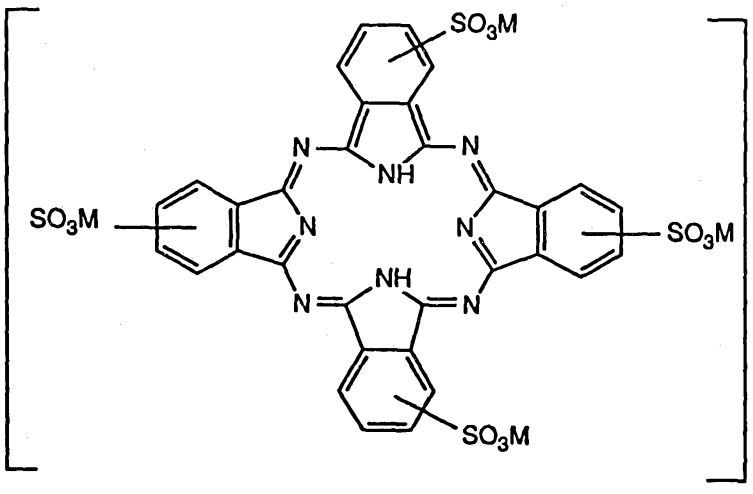
(7)



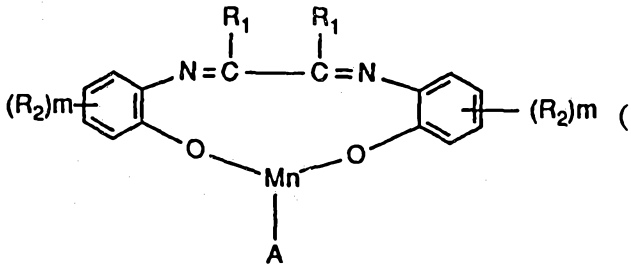
(8)



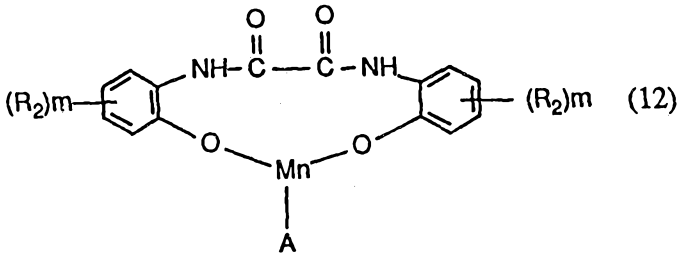
(9)



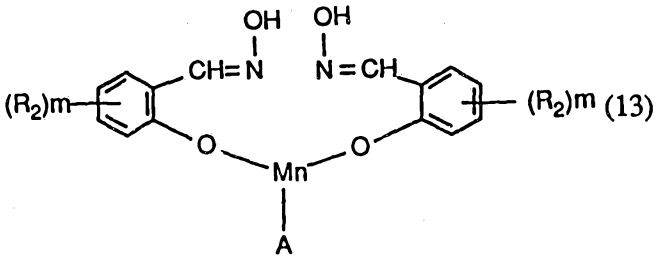
(10)



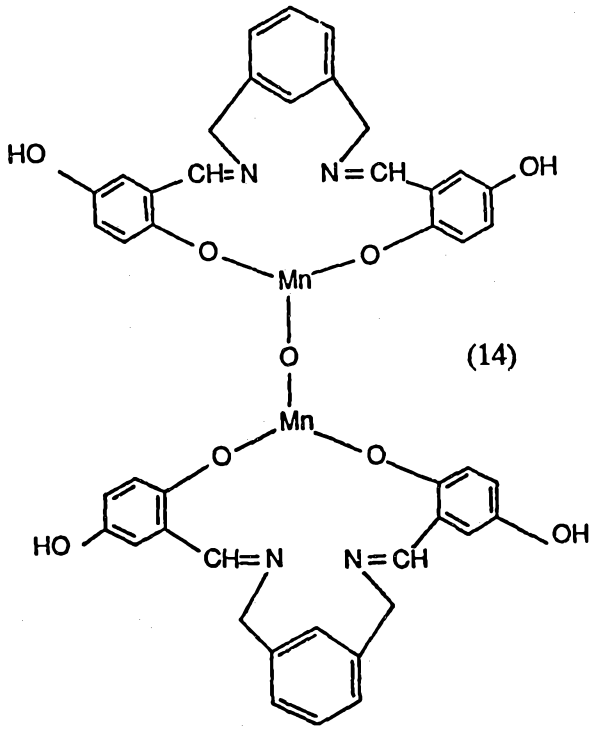
(11)



(12)



(13)



(14)

in which R_1 is hydrogen or optionally substituted alkyl, cycloalkyl or aryl; R_2 is hydrogen, optionally substituted alkyl, optionally substituted alkoxy, halogen, cyano, N(optionally substituted alkyl)$_2$, $N^{\oplus}$(optionally substituted alkyl)$_3$ or a water-solubilising group, especially SO_3M; Y is optionally substituted alkylene, cyclohexylene or arylene; Y_1 is

C_2-C_4 alkylene, optionally interrupted by a nitrogen atom, a 1,4-methanocyclohexylene residue or a phenylene residue optionally substituted by a group SO_3M; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; n is 2 or 3; m is 0 or 1; p is 1 or 2; and A is an anion; with the proviso that R_2 must not be hydrogen unsubstituted alkyl or SO_3M if either m is 1 and Y_1 is optionally substituted alkylene or cycloalkylene.

When one or both of R_1 and R_2 are or contain optionally substituted alkyl, preferred alkyl groups are C_1-C_8-, especially C_1-C_4-alkyl groups. The alkyl groups may be branched or unbranched and may be optionally substituted, e.g. by halogen such as fluorine, chlorine or bromine, by C_1-C_4alkoxy such as methoxy or ethoxy, by phenyl or carboxyl, by C_1 C_4 -alkoxycarbonyl such as acetyl, or by a mono- or di-alkylated amino group.

When R_1 is cycloalkyl, this may also be substituted, e.g. by C_1-C_4-alkyl or C_1-C_4-alkoxy.

When R_1 is optionally substituted aryl, it is preferably a phenyl or naphthyl group each of which may be substituted by C_1-C_4-alkyl, e.g. by methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec.-butyl or tert.-butyl, by C_1-C_4-alkoxy such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec.-butoxy or tert.-butoxy, by halogen such as fluorine, chlorine or bromine, by C_2-C_5-alkanoylamino, such as acetylamino, propionylamino or butyrylamino, by nitro, sulpho or by dialkylated amino.

Optionally substituted alkoxy groups R_2 are preferably C_1-C_8-, especially C_1-C_4-alkoxy groups. The alkoxy groups may be branched or unbranched and may be optionally substituted, e.g. by halogen such as fluorine, chlorine or bromine, by C_1-C_4-alkoxy such as methoxy or ethoxy, by phenyl or carboxyl, by C_1-C_4-alkoxycarbonyl such as acetyl, or by a mono- or di-alkylated amino group.

Halogen atoms R_2 are preferably bromo or, especially, chloro atoms.

N(optionally substituted alkyl)$_2$ groups R_2 are preferably N(optionally substituted C-C_4alkyl)$_2$ groups, especially N(methyl)$_2$ or N(ethyl)$_2$.

$N^{\oplus}$(optionally substituted alkyl)$_3$ groups R_2 and $N^{\oplus}$(optionally substituted C_1-C_4alkyl)$_3$, especially $N^{\oplus}$(methyl)$_3$ or $N^{\oplus}$(ethyl)$_3$.

When Y is alkylene, it is preferably a C_2-C_4- alkylene residue, especially a -CH_2-CH_2-bridge. Y may also be a C_2-C_8-alkylene residue which is interrupted by oxygen or,

AUSTRALIAN PATENT OFFICE

especially, by nitrogen, in particular the $-(CH_2)_3-NH-(CH_2)_3-$ or $-(CH_2)_2-NH-(CH_2)_2$ bridge. When Y is a cyclohexylene residue, it may be a monocyclic cyclohexylene ring or a bicyclic cyclohexylene ring, such as a 1,4-methano-cyclohexylene ring. Arylene residues Y include naphthylene and, especially, phenylene residues, bonded in the 1,2-, 1,3- or 1,4-positions.

When Y is optionally substituted arylene, the substituents are preferably C_1-C_4-alkyl, e.g. methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec.-butyl or tert.-butyl, C_1-C_4-alkoxy such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, sec.-butoxy or tert.-butoxy, halogen such as fluorine, chlorine or bromine, C_2-C_5-alkanoylamino, such as acetylamino, propionylamino or butyrylamino, nitro, an SO_3M or CO_2M group, in which M has its previous significance, or di-C_1-C_4alkylamino.

Anions A include halide, especially chloride, sulphate, nitrate, hydroxy, methoxy, BF_4, PF_6, carboxylate, especially acetate, triflate or tosylate.

With respect to the compounds of formula (1) or (2), preferably R_1 is hydrogen , m is 0 and A is acetate.

In relation to the compounds of formula (3), preferably R_1 is hydrogen, m is 0, n is 2 or 3 and A is acetate.

With respect to the compounds of formula (4), preferred compounds are those in which R_1 is hydrogen, m is 0, n is 2 and A is Cl.

With respect to the compounds of formula (5), preferred compounds are those in which n is 2 and A is chloride.

As to the compounds of formula (6), preferably m is 0, n is 2 and A is acetate.

In relation to the compounds of formula (7), R_1 is preferably hydrogen, Y is preferably 1,2-cyclohexylene, R_2 is preferably C_1-C_4alkyl, especially t-butyl and A is preferably acetate.

With respect to the compounds of formula (8), R_1 is preferably hydrogen, Y_1 is preferably C_2-C_4 alkylene, optionally interrupted by a nitrogen atom, a 1,4-methanocyclohexylene

residue or a phenylene residue substituted by a group SO_3M, in which M has its previous significance, R_2 is preferably hydrogen or a group SO_3M, in which M has its previous significance and A is preferably OH.

In relation to the compounds of formula (9), n is preferably 2 and A is preferably perchlorate.

In relation to compounds of formula (11), R_1 is preferably hydrogen, and with respect to compounds of formula (11), (12) and (13), m is preferably 0 and A is preferably OH.

In each of the compounds of formula (1) to (14), it is preferred that they are used in neutral form, i.e. that M, when present, is other than hydrogen, preferably a cation formed from an alkali metal, in particular sodium, or from an amine.

Moreover, in each of the compounds of formula (1) to (14), the respective benzene rings may contain, in addition to any sulpho group, one or more further substituents such as C_1-C_4-alkyl; C_1-C_4-alkoxy, halogen, cyano or nitro.

The manganese complexes of formula (1) to (6) and (8) to (14) are believed to be new compounds and, as such, form a further aspect of the present invention. They may be produced by known methods, e.g. by the methods analogous to those disclosed in US Patent 4,655,785 relating to similar copper complexes.

The compounds of formula (7) are described, at least in part, in WO 93/03838.

The present invention also provides a detergent composition comprising:
i) 5-90%,preferably 5-70% of A) an anionic surfactant and/or B) a nonionic surfactant;
ii) 5-70%, preferably 5-50%, especially 5-40% of C) a builder;
iii) 0.1-30%, preferably 1-12% of D) a peroxide; and
iv) 0.005-2%, preferably 0.02-1%, especially 0.1-0.5% of E) a compound of formula (1) to (14) as defined above, each by weight, based on the total weight of the detergent.

The detergent may be formulated as a solid; or as a non-aqueous liquid detergent, containing not more than 5, preferably 0-1 wt.% of water, and based on a suspension of a builder in a non-ionic surfactant, as described, e.g., in GB-A-2158454.

Preferably, the detergent is in powder or granulate form.

Such powder or granulate forms may be produced by firstly forming a base powder by spray-drying an aqueous slurry containing all the said components , apart from the components D) and E); then adding the components D) and E) by dry-blending them into the base powder. In a further process, the component E) may be added to an aqueous slurry containing components A), B) and C), followed by spray-drying the slurry prior to dry-blending component D) into the mixture. In a still further process, component B) is not present, or is only partly present in an aqueous slurry containing components A) and C); component E) is incorporated into component B), which is then added to the spray-dried base powder; and finally component D) is dry-blended into the mixture.

The anionic surfactant component A) may be, e.g., a sulphate, sulphonate or carboxylate surfactant, or a mixture of these.

Preferred sulphates are alkyl sulphates having 12-22 carbon atoms in the alkyl radical, optionally in combination with alkyl ethoxy sulphates having 10-20 carbon atoms in the alkyl radical.

Preferred sulphonates include alkyl benzene sulphonates having 9-15 carbon atoms in the alkyl radical.

In each case, the cation is preferably an alkali metal, especially sodium.

Preferred carboxylates are alkali metal sarcosinates of formula $R\text{-}CO(R^1)CH_2COOM^1$ in which R is alkyl or alkenyl having 9-17 carbon atoms in the alkyl or alkenyl radical, R^1 is C_1-C_4 alkyl and M^1 is alkali metal.

The nonionic surfactant component B) may be, e.g., a condensate of ethylene oxide with a C_9-C_{15} primary alcohol having 3-8 moles of ethylene oxide per mole.

The builder component C) may be an alkali metal phosphate, especially a tripolyphosphate; a carbonate or bicarbonate, especially the sodium salts thereof; a silicate; an aluminosilicate; a polycarboxylate; a polycarboxylic acid; an organic phosphonate; or an aminoalkylene poly (alkylene phosphonate); or a mixture of these.

Preferred silicates are crystalline layered sodium silicates of the formula

$NaHSi_mO_{2m+1}.pH_2O$ or $Na_2Si_mO_{2m+1}.pH_2O$ in which m is a number from 1.9 to 4 and p is 0 to 20.

Preferred aluminosilicates are the commercially-available synthetic materials designated as Zeolites A, B, X, and HS, or mixtures of these. Zeolite A is preferred.

Preferred polycarboxylates include hydroxypolycarboxylates, in particular citrates, polyacrylates and their copolymers with maleic anhydride.

Preferred polycarboxylic acids include nitrilotriacetic acid and ethylene diamine tetra-acetic acid.

Preferred organic phosphonates or aminoalkylene poly (alkylene phosphonates) are alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates and diethylene triamine penta methylene phosphonates.

The peroxide component D) may be any organic or inorganic peroxide compound, described in the literature or available on the market, which bleaches textiles at conventional washing temperatures, e.g. temperatures in the range of from 10°C. to 90°C. In particular, the organic peroxides are, for example, monoperoxides or polyperoxides having alkyl chains of at least 3, preferably 6 to 20, carbon atoms; in particular diperoxydicarboxylates having 6 to 12 C atoms, such as diperoxyperazelates, diperoxypersebacates, diperoxyphthalates and/or diperoxydodecanedioates, especially their corresponding free acids, are of interest. It is preferred, however, to employ very active inorganic peroxides, such as persulphate, perborate and/or percarbonate. It is, of course, also possible to employ mixtures of organic and/or inorganic peroxides. Peroxides can have different crystalline forms and/or different degrees of hydration. They may be used in admixture with other organic or inorganic salts, thereby improving their stability to storage.

The addition of the peroxides to the detergent is effected, in particular, by mixing the components, for example by means of screw-metering systems and/or fluidized bed mixers.

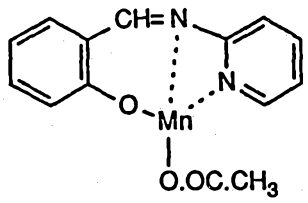
The detergents may contain, in addition to the combination according to the invention, one

or more of fluorescent whitening agents, such as a bis-triazinylamino-stilbene-disulphonic acid, a bis-triazolyl-stilbene-disulphonic acid, a bis-styryl-biphenyl, a bis-benzofuranylbiphenyl, a bis-benzoxalyl derivative, a bis-benzimidazolyl derivative, a coumarine derivative or a pyrazoline derivative; soil suspending agents, for example sodium carboxymethylcellulose; salts for adjusting the pH, for example alkali or alkaline earth metal silicates; foam regulators, for example soap; salts for adjusting the spray drying and granulating properties, for example sodium sulphate; perfumes; and also, if appropriate, antistatic and softening agents; such as smectite clays; enzymes, such as amylases; photobleaching agents; pigments; and/or shading agents. These constituents should, of course, be stable to the bleaching system employed.

A particularly preferred detergent co-additive is a polymer known to be useful in preventing the transfer of labile dyes between fabrics during the washing cycle. Preferred examples of such polymers are polyvinyl pyrrolidones, optionally modified by the inclusion of an anionic or cationic substituent, especially those having a molecular weight in the range from 5000 to 60,000, in particular from 10,00 to 50,000. Preferably, such polymer is used in an amount ranging from 0.05 to 5%, preferably 0.2-1.7% by weight, based on the weight of the detergent.

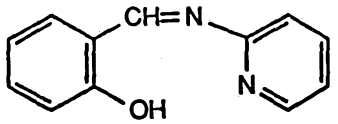
The following Examples serve to illustrate the invention; parts and percentages are by weight, unless otherwise stated.

Example 1



(101)

A) To a solution of 18.8 g. of 2-aminopyridine in 300 ml. of ethanol, there are added 24.4 g. of salicylaldehyde. The mixture is heated to 70-75°C. and stirred for 7 hours. The mixture is concentrated to one third of its volume and then cooled to 5°C., whereupon an orange product having the formula:



(101a)

crystallised out. The product is filtered off with suction and allowed to dry in the air, giving a yield of 25.5 g. (65% of theory).

Elemental analysis of the compound having the formula (101a) and having the empirical formula $C_{12}H_{10}N_2O$ gives:

Req.% C 72.71; H 5.08; N 14.13.

Found % C 72.6; H 5.1; N 14.1.

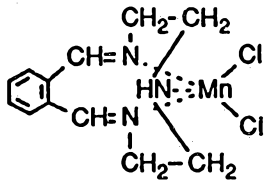
B) To a solution of 5.9 g. of the compound of formula (101a) obtained in Part A), in 200 ml. of ethanol, there are added 8.5 g. of manganese-III-acetate dihydrate. The resulting dark brown solution is stirred for 5 hours at 60-65°C. and evaporated to dryness. The residue is dried in vacuum giving a yield of 6.3 g. (68% of theory) of a light brown compound having the formula (101).

Elemental analysis of the compound having the formula (101) and having the empirical formula $C_{14}H_{12}MnN_2O_3 . CH_3COOH$ gives:

Req.% C 49.48; H 4.38; N 7.22; Mn 14.17.

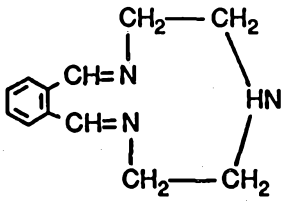
Found % C 50.18; H 4.45; N 7.40; Mn 14.4.

Example 2



(102)

A) To a solution of 26.8 g. phthaldialdehyde in 1000 ml. of ethanol there are added 21.5 ml. of diethylenetriamine and the mixture is stirred for 20 hours at 25°C. The resulting solution becomes brown-green in colour and is evaporated to dryness giving 40 g. (100% theory) of a thick brown liquid having the formula:



(102a)

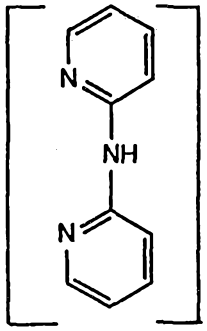
B) To a solution of 19.8 g. of manganese-II-chloride tetrahydrate in 250 ml. of ethanol, there is added a solution of 20.1 g. of the product of formula (102a) in 250 ml. of ethanol. An ochre yellow suspension is formed and this is stirred for 18 hours at 25°C. The product is filtered off with suction, washed with ethanol and dried in vacuum at 25°C. giving 28 g. (85% theory) of an ochre yellow of formula (102).

Elemental analysis of the compound having the formula (102) and having the empirical formula $C_{12}H_{14}Cl_2MnN_3$ gives:

Req.% C 37.81; H 5.55; N 11.02; Cl 18.60; Mn 14.41.

Found % C 38.0; H 5.0; N 10.5; Cl 19; Mn 15.4.

Example 3

$3\ Mn(CH_3COO)_2\ .\ 2$  (103)

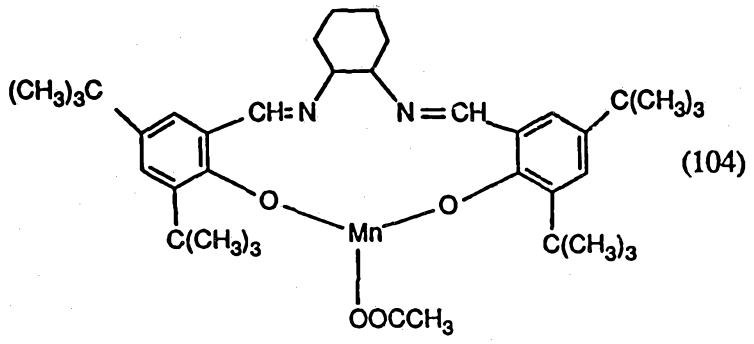
To a solution of 5.1 g. of 2,2'-dipyridylamine in 50 ml. of ethanol there are added 7.4 g. of manganese-II-acetate tetrahydrate and the mixture is stirred for 18 hours at 25°C. The product is filtered off with suction, washed with methanol and dried in vacuum at 25°C. giving 6.6 g. (58% theory) of a white product having the formula (103).

Elemental analysis of the compound having the formula (103) and having the empirical formula $C_{32}H_{36}Mn_3N_6O_{12}$ gives:

Req.% C 44.62; H 4.21; N 9.76; Mn 19.13.

Found % C 44.70; H 4.15; N 9.72; Mn 19.8.

Example 4



(104)

8.2 g. of 1,2-bis(3,5-di-tert.butylsalicylidamino)cyclohexane are added to 400 ml. of ethanol, the mixture is heated to 65°C. and 3.7 g. of manganese-II-acetate tetrahydrate are added to the yellow suspension. After a short time, a dark brown solution is formed which

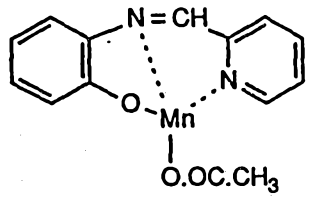
is stirred for 15 hours and then evaporated to dryness. 9.5 g. (92.8% theory) of a dark brown powder having the formula (104) are obtained.

Elemental analysis of the compound having the formula (104) and having the empirical formula $C_{38}H_{55}MnN_2O_4$. 1.33 H_2O gives:

Req.% C 66.85; H 8.43; N 4.10; Mn 8.05.

Found % C 66.98; H 8.53; N 4.00; Mn 7.82.

Example 5



(105)

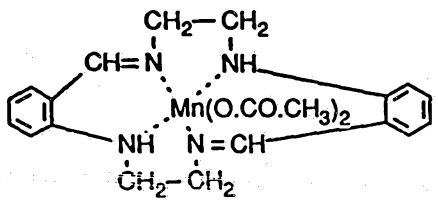
10.9 g. of o-aminophenol and 10.7 g. of pyridine-2-aldehyde are stirred in 200 ml. of ethanol for 5 hours at 60-65°C. The solution is then treated with 24.5 g. of manganese-II-acetate tetrahydrate and stirred for 5 hours at 60-65°C. The solution is evaporated and the residue is dried in vacuum giving 31 g. (95% theory) of a red-brown product having the formula (105).

Elemental analysis of the compound having the formula (105) and having the empirical formula $C_{14}H_{12}MnN_2O_3$. 0.83 H_2O gives:

Req.% C 51.58; H 4.22; N 8.59; Mn 16.87.

Found % C 51.76; H 3.91; N 8.11; Mn 16.80.

Example 6

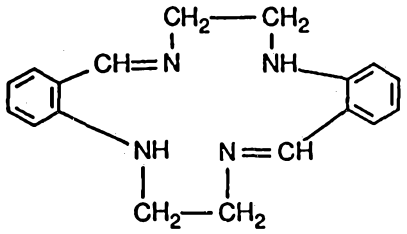


(106)

20A) To a solution of 405 ml. of diaminoethane in 1000 ml. of toluene there are added 20

ml. of formic acid and 63.4 g. of copper dust. The suspension is heated to 100°C. and is treated, dropwise, over 2 hours, with a solution of 111 ml. of o-chlorobenzaldehyde in 115 ml. of toluene. After 4 hours at 100°C., the mixture is cooled to 75°C. and some copper dust is filtered off.

The filtrate forms two phases. The upper toluene phase is separated and concentrated to 100 ml. This concentrate is diluted with 200 ml. of ethanol and allowed to stand for 48 hours at 25°C. The product which crystallises out is filtered with suction and dried in vacuum at 40°C. giving 24 g. (16% theory) of a yellow product having the formula:



(106a)

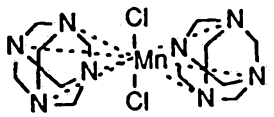
B) 5.8 g. of the compound of formula (106a) obtained in Part A) and 5 g. of manganese-II-acetate tetrahydrate are stirred for 12 hours in 200 ml. of ethanol, filtered with suction, washed with ethanol and dried in vacuum, giving 7.5 g. of the compound of formula (106).

Elemental analysis of the compound having the formula (106) and having the empirical formula $C_{22}H_{26}MnN_4O_4$. 0.14 MnO_2 gives:

Req.% C 55.30; H 5.48; N 11.72; Mn 13.12.

Found % C 55.34; H 5.55; N 11.80; Mn 12.70.

Example 7



(107)

To a solution of 19.8 g. of manganese-II-chloride in 200 ml. of methanol there are added 14 g. of hexamethylenetetramine. After stirring at 25°C. for 20 hours, the precipitated product is filtered with suction and dried in vacuum at 25°C., giving 18.5 g. (91% theory)

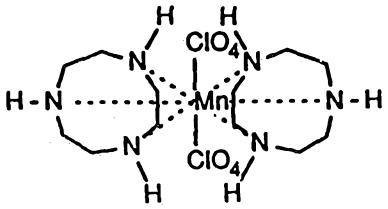
of a light grey product having the formula (107).

Elemental analysis of the compound having the formula (107) and having the empirical formula $C_{12}H_{24}Cl_2MnN_8$ 2 H_2O gives:

Req.% C 32.59; H 6.38; N 25.34; Cl 16.03; Mn 12.42.

Found % C 32.2; H 6.5; N 24.8; Cl 16.2; Mn 12.4.

Example 8



(108)

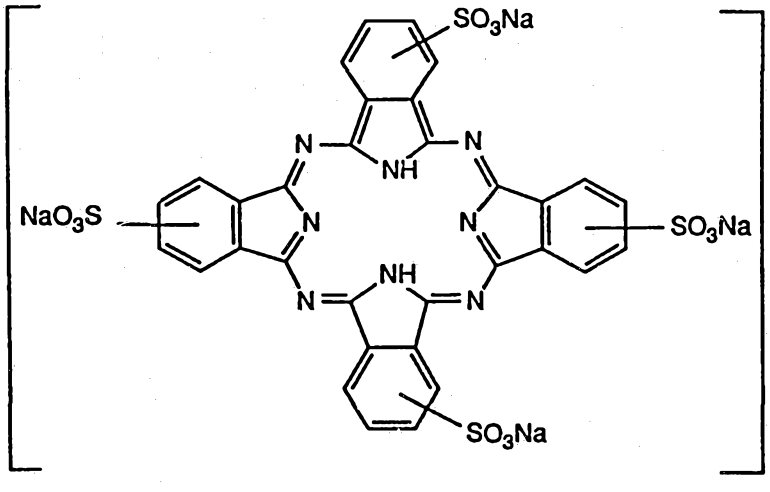
To a solution of 3 g. of triazacyclononane in 80 ml. of methanol there are added 2 g. of manganese perchlorate hexahydrate. A white suspension is formed immediately. After 30 minutes, 1 g. of sodium acetate is added and the mixture is stirred for 24 hours at 25°C. The product is filtered with suction, washed with methanol and dried in vacuum at 25°C., giving 1.8 g. (65% theory) of a white product having the formula (108).

Elemental analysis of the compound having the formula (108) and having the empirical formula $C_{12}H_{30}Cl_2MnN_6O_8$ gives:

Req.% C 28.12; H 5.86; N 16.41; Cl 13.87; Mn 10.74.

Found % C 28.1; H 6.2; N 16.3; Cl 13.6; Mn 11.0.

Example 9



(109)

To a solution of 13.8 g. of phthalocyanine tetrasulphonic acid in 140 ml. of water there are added 4.2 g. of manganese-III-acetate dihydrate. The mixture is heated to 70-75°C. and stirred for 12 hours. 20 g. of sodium chloride are added, the mixture is stirred for a further 6 hours, cooled to 5°C. and filtered with suction. The material filtered off is dissolved in 200 ml. of water and dialysed for 40 hours. The solution remaining is evaporated to dryness and the residue is dried in vacuum, giving 3.5 g. (20% theory) of a black product having the formula (109).

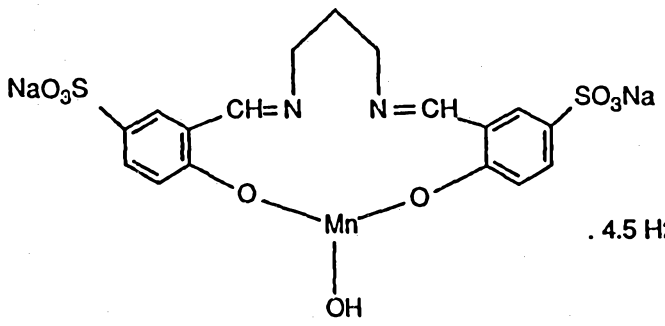
Elemental analysis of the compound having the formula (109) and having the empirical formula $C_{64}H_{40}Mn_3N_{16}O_{24}S_8$ .22 H_2O gives:

Req.% C 31.78; H 3.50; N 9.27; S 10.61; Mn 6.81.

Found % C 32.1; H 3.2; N 9.4; S 10.7; Mn 6.79.

Example 10

Using a procedure similar to that described in Example 4, the compound having the formula (110) is obtained:



(110)

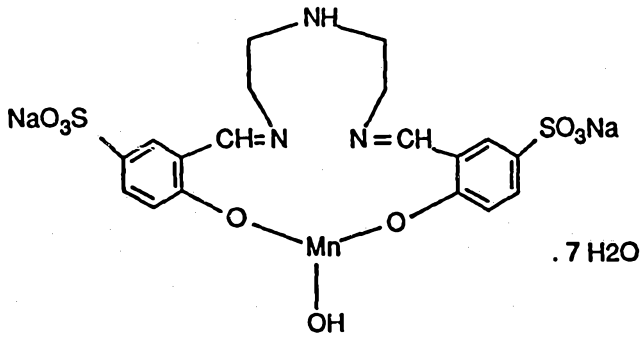
Elemental analysis of the compound having the formula (110) and having the empirical formula $C_{17}H_{15}MnN_2Na_2O_9S_2$ .4.5 H_2O gives:

Req.% C 32.57; H 3.77; N 4.44; S 10.22; Mn 8.7.

Found % C 32.51; H 3.75; N 4.38; S 9.97; Mn 7.6.

Example 11

Using a procedure similar to that described in Example 4, the compound having the formula (111) is obtained:



(111)

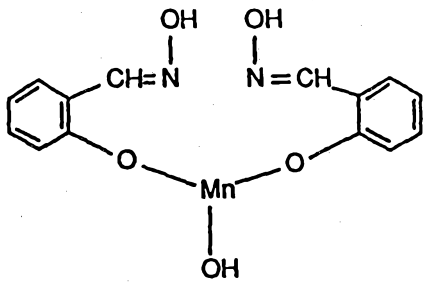
Elemental analysis of the compound having the formula (111) and having the empirical formula $C_{18}H_{18}MnN_3Na_2O_9S_2$ .7 H_2O gives:

Req.% C 30.39; H 4.93; N 5.91; S 9.01; Mn 7.72.

Found % C 30.50; H 4.39; N 5.96; S 8.98; Mn 7.36.

Example 12

Using a procedure similar to that described in Example 4, the compound having the formula (112) is obtained:



(112)

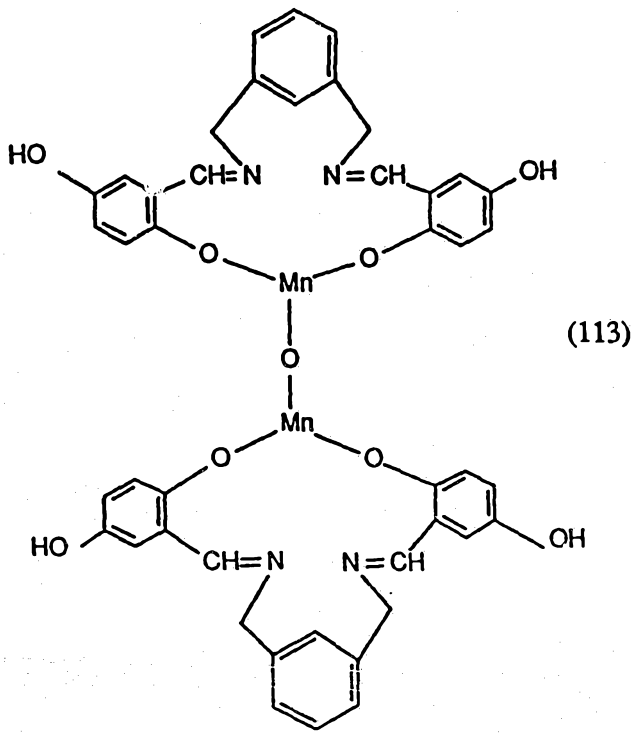
Elemental analysis of the compound having the formula (112) and having the empirical formula $C_{14}H_{13}MnN_2O_5$ gives:

Req.% C 48.85; H 3.81; N 8.13; Mn 15.96.

Found % C 48.44; H 3.82; N 8.07; Mn 16.20.

Example 13

Using a procedure similar to that described in Example 4, the compound having the formula (113) is obtained:



(113)

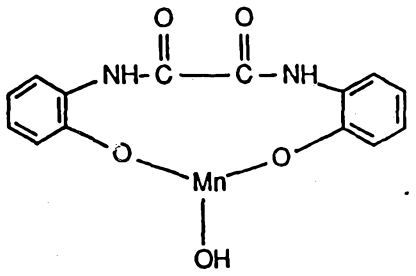
Elemental analysis of the compound having the formula (113) and having the empirical formula $C_{44}H_{36}Mn_2N_2O_{10}.8\ H_2O$ gives:

Req.% C 51.07; H 5.06; N 5.41; Mn 10.61; O 27.83.

Found % C 51.18; H 4.35; N 5.48; Mn 10.3; O 28.69.

Example 14

Using a procedure similar to that described in Example 4, the compound having the formula (114) is obtained:



(114)

. 1.5 H2O

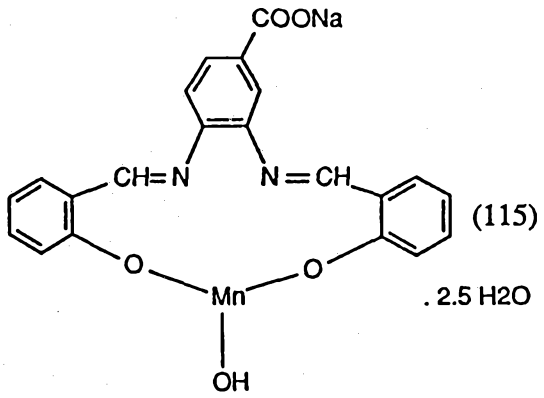
Elemental analysis of the compound having the formula (114) and having the empirical formula $C_{14}H_{11}MnN_2O_5.1.5\ H_2O$ gives:

Req.% C 45.54; H 3.82; N 7.58; Mn 14.80.

Found % C 45.57; H 4.04; N 7.63; Mn 13.70.

Example 15

Using a procedure similar to that described in Example 4, the compound having the formula (115) is obtained:



Elemental analysis of the compound having the formula (115) and having the empirical formula $C_{21}H_{14}MnN_2NaO_5.2.5\ H_2O$ gives:

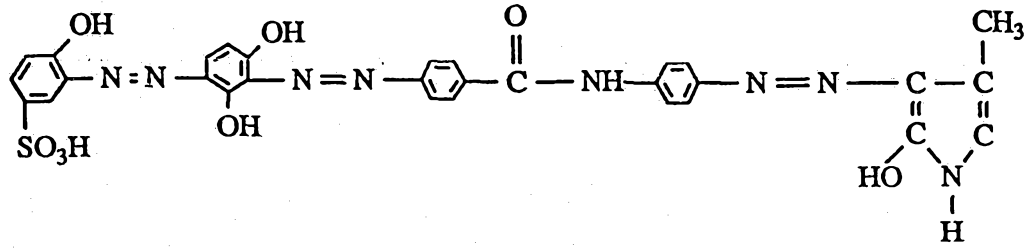
Req.% C 50.72; H 3.85; N 5.63; Mn 12.04; O 24.1.

Found % C 50.74; H 3.54; N 5.67; Mn 12.9; O 24.2.

Examples 16 to 18

The re-uptake of dyes, which have become detached from a coloured article during the washing process and re-absorbed on to goods which are also being washed and which are thereby discoloured, is evaluated using a test dye, as follows:

The following commercial brown dyestuff is tested at a concentration of 10 mg per litre of wash liquor:



There is then added to this wash liquor, with stirring, in a concentration of 7.5 g. per litre of tap water, a detergent having the following composition:

6 % Sodium alkylbenzenesulfonate (®Marlon A375);

5 %	Ethoxylated C_{14}-C_{15} fatty alcohol (7 moles EO);
3 %	Sodium soap;
30 %	Zeolite A;
7.5 %	Sodium carbonate;
5 %	Sodium metasilicate ($5.H_2O$);
43.5 %	Sodium sulphate.

The pH of the wash liquor is adjusted to pH 11 by the addition of the necessary amount of 0.1N aqueous NaOH solution.

The bath is then tested in a "®Linitest" beaker for 20 minutes at 30°. After the addition, with stirring, directly before the treatment, of x% (see Table 1 below) of sodium perborate monohydrate, and/or of y% (see Table 1 below) of a compound of formula (101), (102) or (103), each based on the weight of the above detergent, a bleached cotton fabric, in an amount of 50g. per litre of wash bath, is also added.

After the wash treatment, over 20 minutes at 30°C., the fabric pieces are rinsed, dried and quickly ironed and their brightness Y is determined using an ICS SF 500 Spectrophotometer.

The difference between the fabric washed without the addition of a dye, and the fabric washed with the addition of the brown dye, viz. "ΔY without bleach system" serves as a control rating for the discolouration.

The effectivity of a bleaching system is determined from the equation:

$$\text{Effectivity in \%} = \frac{\Delta Y \text{ without bleach} - \Delta Y \text{ with bleach}}{\Delta Y \text{ without bleach}} \times 100$$

The results obtained are set out in Table 1:

Table 1

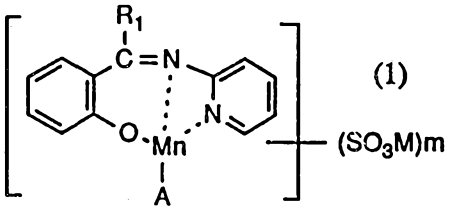
Example	Perborate	Compound (101)	Effectivity
	x%	y%	
Control	0	0	0%
Control	2	0	8%
16	2	0.2	69%

Similar results are obtained when the compound of formula (101) is replaced by a compound having one of the formulae (102; Effectivity 72%; Example 17) or (103; Effectivity 70%; Example 18).

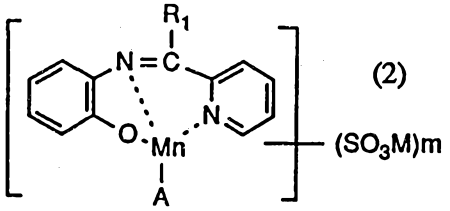
Claims

The claims defining the invention are as follows:

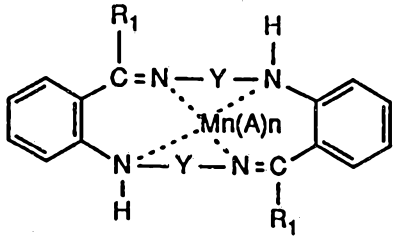
1. A process for inhibiting the re-absorption of migrating dyes in the wash liquor, comprising introducing into a wash liquor containing a peroxide-containing detergent, from 0.5 to 150 mg, per litre of wash liquor, of one or more compounds having the formula (1), (2), (3), (4), (5), (6), (7), (8), (9), (10), (11), (12), (13) or (14):



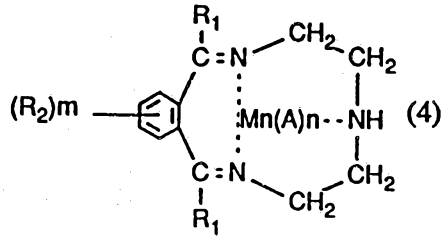
(1)



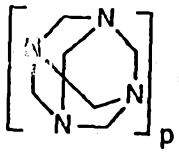
(2)



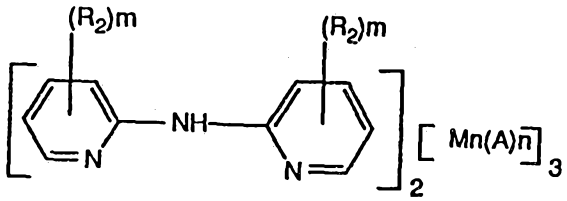
(3)



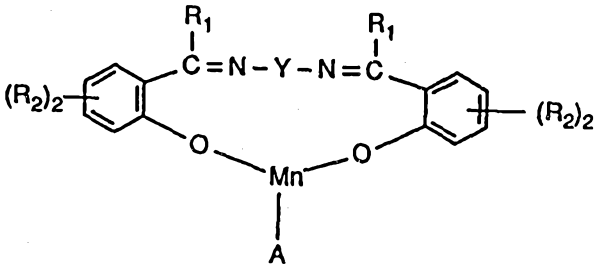
(4)


Mn(A)n
p

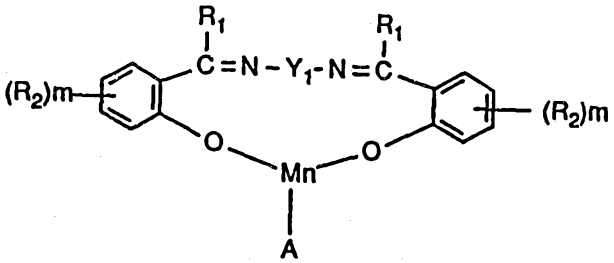
(5)


(R2)m
(R2)m
NH
N
N
Mn(A)n
2
3

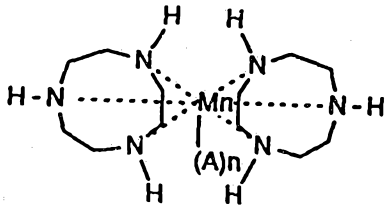
(6)


R1
R1
C=N-Y-N=C
(R2)2
(R2)2
O
O
Mn
A

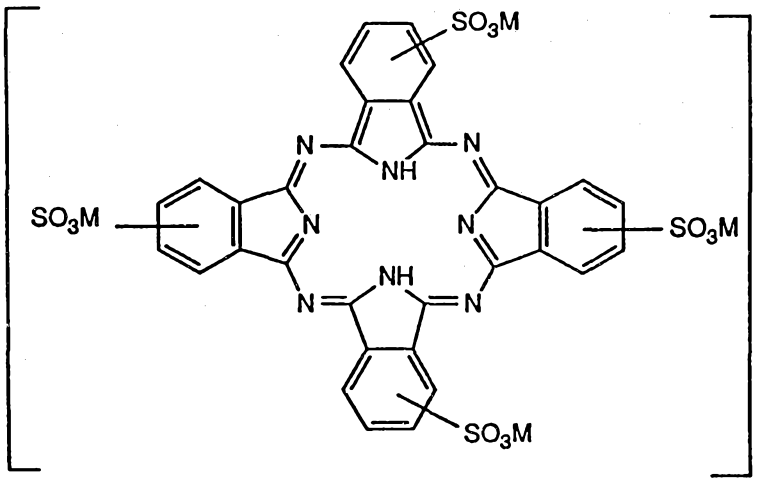
(7)


R1
R1
C=N-Y1-N=C
(R2)m
(R2)m
O
O
Mn
A

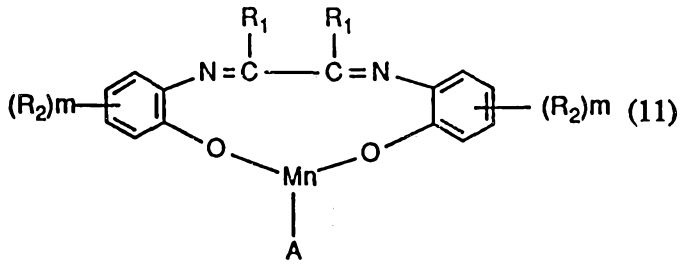
(8)


H
H
N
N
H-N
N-H
Mn
N
N
(A)n
H
H

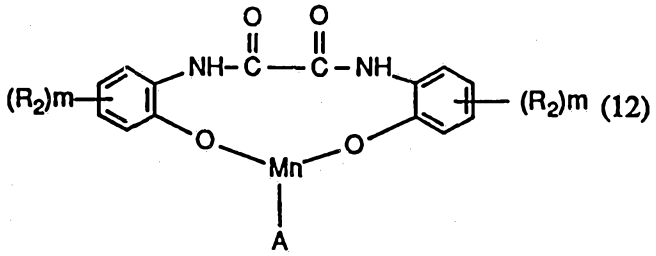
(9)


SO3M
N
NH
N
N
N
SO3M
SO3M
N
NH
N
N
SO3M
Mn3
2

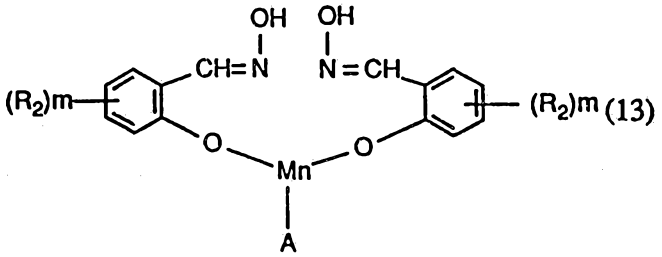
(10)


R1
R1
N=C
C=N
(R2)m
(R2)m
O
O
Mn
A

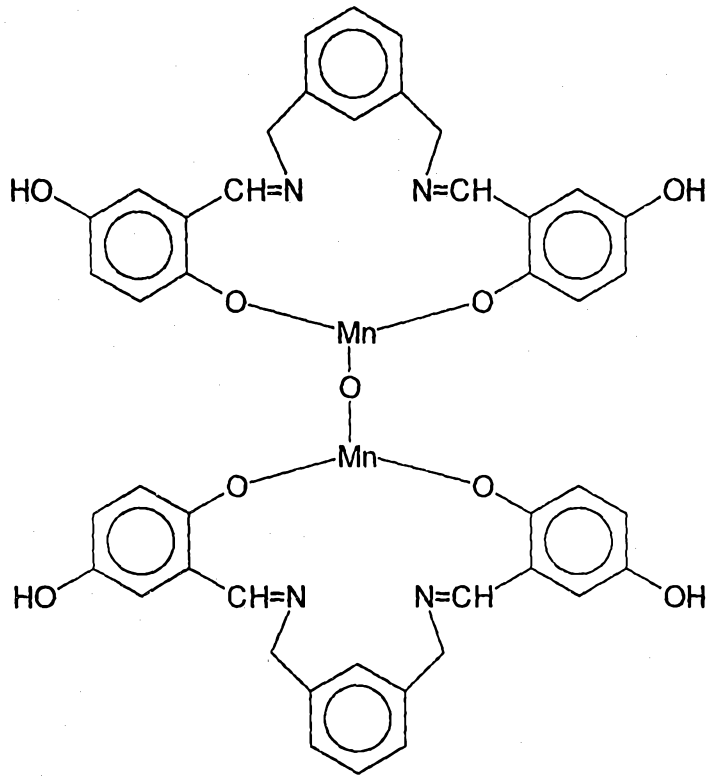
(11)


O
O
NH-C
C-NH
(R2)m
(R2)m
O
O
Mn
A

(12)


OH
OH
CH=N
N=CH
(R2)m
(R2)m
O
O
Mn
A

(13)



(14)

in which R_1 is hydrogen or optionally substituted alkyl, cycloalkyl or aryl; R_2 is hydrogen, optionally substituted alkyl, optionally substituted alkoxy, halogen, cyano, N(optionally substituted alkyl)$_2$, $N^{\oplus}$(optionally substituted alkyl)$_3$ or a water-solubilising group; Y is optionally substituted alkylene, cyclohexylene or arylene; Y_1 is C_2-C_4 alkylene, optionally interrupted by a nitrogen atom, a 1,4-methanocyclohexylene residue or a phenylene residue optionally substituted by a group SO_3M; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; n is 2 or 3; m is 0 or 1; p is 1 or 2; and A is an anion; with the proviso that R_2 must not be hydrogen, unsubstituted alkyl or SO_3M if either m is 1 and Y_1, is optionally substituted alkylene or cycloalkylene.

2. A process according to claim 1 in which from 1.5 to 75mg, per litre of wash liquor of one or more compounds having the formula (1), (2), (3), (4), (5), (6), (7), (8), (9), (10), (11), (12), (13) or (14) is introduced into the wash liquor.

3. A process according to claim 2 in which from 7.5 to 40mg, per litre of wash liquor of one or more compounds having the formula (1), (2), (3), (4), (5), (6), (7), (8), (9), (10), (11), (12), (13) or (14) is introduced into the wash liquor.

4. A process according to claim 1 in which the water-solubilising group R_2 is SO_3M in

AUSTRALIAN PATENT OFFICE

which M is as defined in claim 1.

5. A process according to any of the preceding claims in which a compound of formula (1) or (2) is used in which R_1 is hydrogen, m is 0 and A is acetate.

6. A process according to any of claims 1 to 4 in which a compound of formula (3) is used in which R_1 is hydrogen, m is 0, n is 2 or 3 and A is acetate.

7. A process according to any of claims 1 to 4 in which a compound of formula (4) is used in which R_1 is hydrogen, m is 0, n is 2 and A is chloride.

8. A process according to any of claims 1 to 4 in which a compound of formula (5) is used in which n is 2 and A is chloride.

9. A process according to any of claims 1 to 4 in which a compound of formula (6) is used in which m is 0, n is 2 and A is acetate.

10. A process according to any of claims 1 to 4 in which a compound of formula (7) is used in which R_1 is hydrogen, Y is 1,2-cyclohexylene, R_2 is C_1-C_4alkyl and A is acetate.

11. A process according to any of claims 1 to 4 in which a compound of formula (8) is used in which R_1 is hydrogen, Y_1 is C_2-C_4 alkylene, optionally interrupted by a nitrogen atom, or Y_1 is a 1,4-methanocyclohexylene residue or a phenylene residue substituted by a group SO_3M in which M is as defined in claim 1, R_2 is hydrogen or a group SO_3M, in which M is as defined in claim 1 and A is OH.

12. A process according to any of claims 1 to 4 in which a compound of formula (9) is used in which n is 2 and A is perchlorate.

13. A process according to any claims 1 to 4 in which a compound of formula (11) is used in which R_1 is hydrogen, m is 0 and A is OH.

14. A process according to any of claims 1 to 4 in which a compound of formula (12) or (13) is used in which m is 0 and A is OH.

15. A detergent composition comprising:

AUSTRALIAN PATENT OFFICE

i) 5-90% of A) an anionic surfactant and/or B) a nonionic surfactant;
ii) 5-70% of C) a builder;
iii) 0.1-30% of D) a peroxide; and
iv) 0.005-2% of E) a compound of formula (1) to (14) as defined in claim 1, each by weight, based on the total weight of the detergent.

16. A composition according to claim 15 comprising:
i) 5-70% of A) an anionic surfactant and/or B) a nonionic surfactant;
ii) 5-50% of C) a builder;
iii) 1-12% of D) a peroxide; and
iv) 0.02-1% of E) a compound of formula (1) to (14) as defined in claim 1, each by weight, based on the total weight of the detergent.

17. A composition according to claim 16 comprising:
i) 5-70% of A) an anionic surfactant and/or B) a nonionic surfactant;
ii) 5-40% of C) a builder;
iii) 1-12% of D) a peroxide; and
iv) 0.1-0.5% of E) a compound of formula (1) to (14) as defined in claim 1, each by weight, based on the total weight of the detergent.

18. A composition according to any of claims 15 to 17 comprising a combination of two or more of the compounds of formula (1) to (14) as defined in claim 1.

19. A composition according to any of claims 15 to 18 comprising 0.5-5% by weight of a polymer useful in preventing the transfer of labile dyes between fabrics during a washing cycle.

20. A composition according to claim 19 comprising 0.2-1.7% of the polymer.

21. A composition according to claim 19 or 20 in which the polymer is a polyvinylpyrrolidone optionally containing an anionic or cationic substituent.

22. A composition according to any of claims 15 to 21 in which the detergent is in powder or granulate form.

23. A composition according to any of claims 15 to 22 in which the detergent is in liquid

form and contains 0-5% water.

24. A composition according to claim 23 in which the detergent is in liquid form and contains 0-1% water.

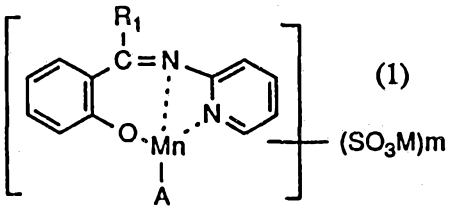
25. A process for the production of a detergent as claimed in claim 22 in which the components of the detergent are mixed in dry form.

26. A process for the production of a detergent as claimed in claim 22 in which a base powder is produced by spray-drying an aqueous slurry which contains all the components defined in claim 15, apart from the components D) and E); and then adding the components D) and E) by dry-blending them into the base powder.

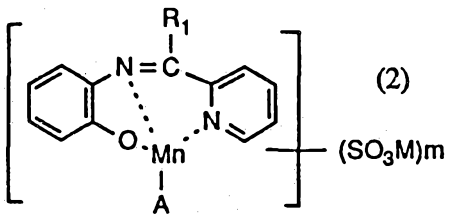
27. A process for the production of a detergent as claimed in claim 22 in which the component E) is added to the slurry containing components A), B) and C), which slurry is then spray-dried before component D) is dry-blended into the mixture.

28. A process for the production of a detergent as claimed in claim 22 in which component B) is not present, or is only partly present in a slurry containing components A) and C); the component E) is incorporated into component B), which is then added to the spray-dried base powder;and finally component D) is dry-blended into the mixture.

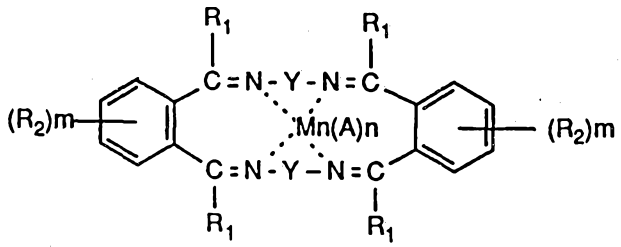
29. A compound having the formula (1), (2), (3), (4), (5), (6), (8), (9), (10), (11), (12), (13) or (14):

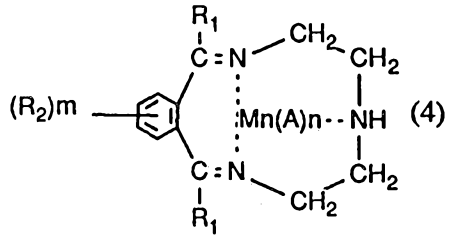


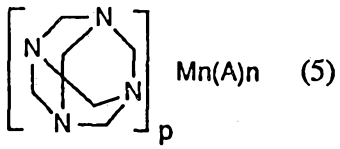
(1)

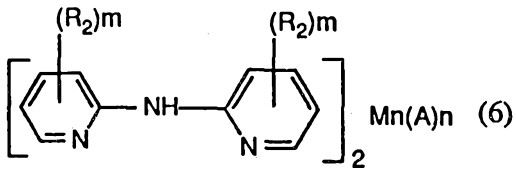


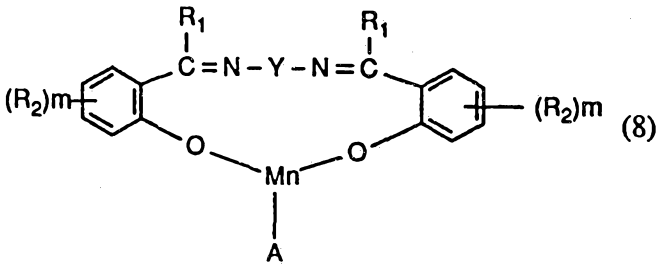
(2)

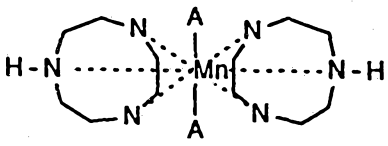

(3)

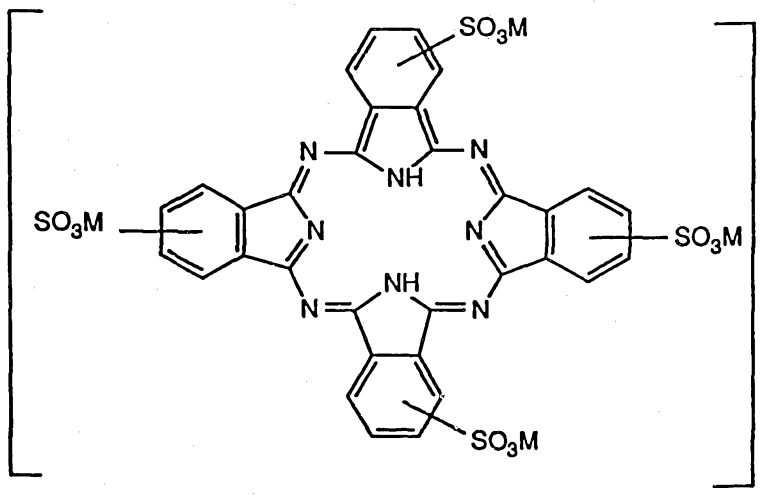

(4)


(5)

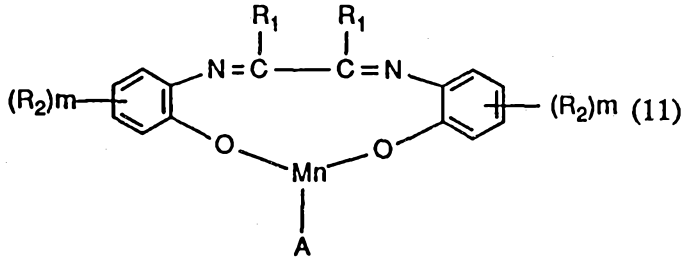

(6)


(8)

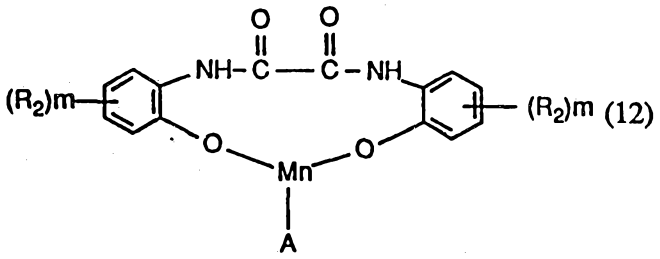

(9)


SO3M
N
NH
N
SO3M
N
N
SO3M
Mn3
N
NH
N
SO3M
2

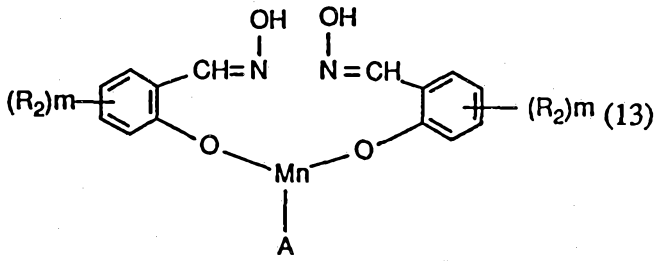
(10)


R1
R1
N=C
C=N
(R2)m
(R2)m
O
O
Mn
A

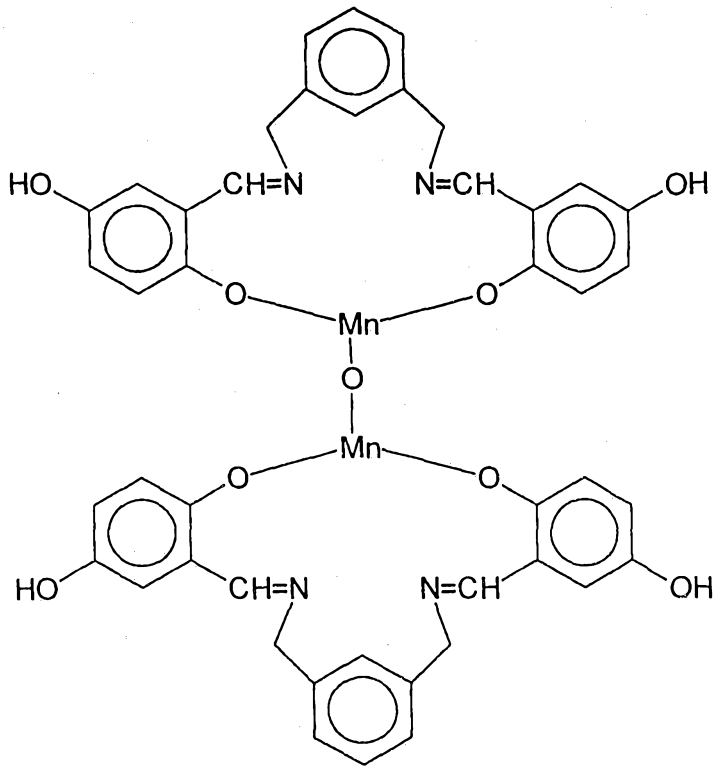
(11)


O
O
NH-C
C-NH
(R2)m
(R2)m
O
O
Mn
A

(12)


OH
OH
CH=N
N=CH
(R2)m
(R2)m
O
O
Mn
A

(13)



(14)

in which R_1 is hydrogen or optionally substituted alkyl, cycloalkyl or aryl; R_2 is hydrogen, optionally substituted alkyl, optionally substituted alkoxy, halogen, cyano, N(optionally substituted alkyl)$_2$, $N^{\oplus}$(optionally substituted alkyl)$_3$ or a water-solubilising group; Y is optionally substituted alkylene, cyclohexylene or arylene; Y_1 is C_2-C_4 alkylene, optionally interrupted by a nitrogen atom, a 1,4-methanocyclohexylene residue or a phenylene residue optionally substituted by a group SO_3M; M is hydrogen, an alkali metal atom, ammonium or a cation formed from an amine; n is 2 or 3; m is 0 or 1, p is 1 or 2; and A is an anion; with the proviso that R_2 must not be hydrogen, unsubstituted alkyl or SO_3M if either m is 1 and Y_1 is optionally substituted alkylene or cycloalkylene.

AUSTRALIAN PATENT OFFICE

30. A process for inhibiting the re-absorption of migrating dyes in the wash liquor, comprising introducing into a wash liquor containing a peroxide-containing detergent, substantially as hereinbefore described with reference to any one of the Examples.

31. A detergent composition, substantially as hereinbefore described with reference to any one of the Examples.

32. A dye migration inhibiting compound, substantially as hereinbefore described with reference to any one of the Examples.

Dated 23 November, 1995

~~Ciba-Geigy AG~~
Ciba Specialty Chemicals Holding Inc

Patent Attorneys for the Applicant/Nominated Person

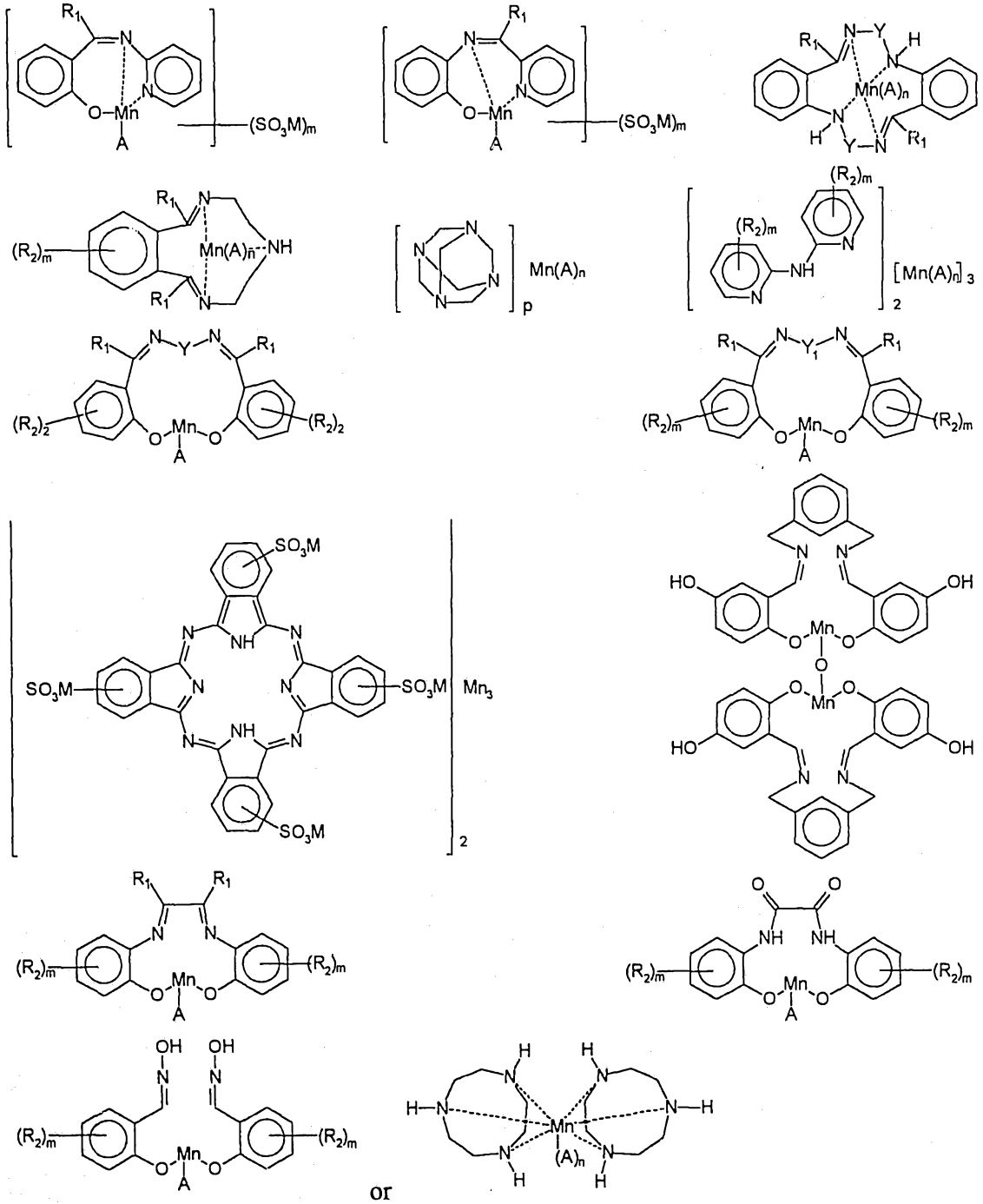
SPRUSON & FERGUSON

AUSTRALIAN PATENT OFFICE SEC 113

Inhibition of Dye Migration

Abstract

A process is described for inhibiting the re-absorption of migrating dyes in the wash liquor, comprising introducing into a wash liquor contairiing a peroxide-containing detergent, from 0.5 to 150mg/L of wash liquor, of one or more compounds



or

in which R_1 is H or optionally substituted alkyl, cycloalkyl or aryl; R_2 is H, optionally substituted alkyl or alkoxy, halo, CN, N(optionally substituted alkyl)$_2$, $N^{\oplus}$(optionally substituted alkyl)$_3$ or a water-solubilising group; Y is optionally substituted alkylene, cyclohexylene or arylene; Y_1 is alkylene, optionally interrupted by N, a 1,4-methanocyclohexylene or optionally substituted phenylene; M is H, an alkali metal, NH_4^+ or an amine cation; n is 2 or 3; m is 0 or 1; p is 1 or 2; and A is an anion. The compounds are new compounds. The compounds do not exhaust on cotton, polyamide or polyester fibres, so that the compounds cannot lead to fibre discolouration.