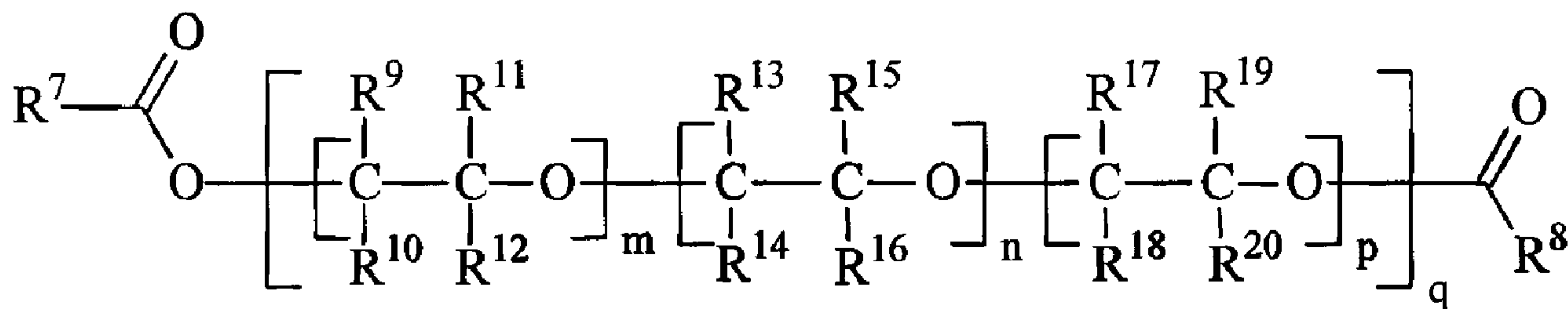




(86) Date de dépôt PCT/PCT Filing Date: 2000/05/30
(87) Date publication PCT/PCT Publication Date: 2001/01/04
(45) Date de délivrance/Issue Date: 2009/11/24
(85) Entrée phase nationale/National Entry: 2001/11/26
(86) N° demande PCT/PCT Application No.: GB 2000/002067
(87) N° publication PCT/PCT Publication No.: 2001/000889
(30) Priorité/Priority: 1999/06/24 (GB9914669.8)

(51) Cl.Int./Int.Cl. *C22B 3/30* (2006.01),
C22B 15/00 (2006.01), *C22B 3/00* (2006.01),
C22B 3/26 (2006.01)
(72) Inventeurs/Inventors:
CUPERTINO, DOMENICO CARLO, GB;
SUGARMAN, ALAN DAVID, GB
(73) Propriétaire/Owner:
CYTEC TECHNOLOGY CORP., US
(74) Agent: SMART & BIGGAR

(54) Titre : COMPOSITION ET PROCEDE D'EXTRACTION PAR SOLVANTS DE METAUX AU MOYEN D'AGENTS
D'EXTRACTION ALDOXIME OU CETOXIME
(54) Title: COMPOSITION AND PROCESS FOR THE SOLVENT EXTRACTION OF METALS USING ALDOXIME OR
KETOXIME EXTRACTANTS



Formula (2)

(57) **Abrégé/Abstract:**

A solvent extraction composition is provided which comprises one or more orthohydroxyaryldoxime or orthohydroxyarylketoimine and at least one dialkyl ester of an optionally substituted ethylene or polyethylene glycol and preferably a water immiscible organic solvent. The orthohydroxyaryldoximes, or orthohydroxyarylketoimines commonly are of Formula (1), wherein R¹ is hydrogen or a hydrocarbonyl group, and R² is an ortho-hydroxyaryl group; and the dialkyl esters of an optionally substituted ethylene or polyethylene glycol commonly are of Formula (2), wherein R⁷ and R⁸ are each independently an optionally substituted alkyl group; R⁹ to R²⁰ are each independently hydrogen or optionally substituted hydrocarbonyl; m, n and p are each independently 0, 1, 2, 3 or 4 provided that m+n+p is greater than or equal to 1; and q is 1, 2 or 3. Preferred orthohydroxyaryldoximes are 5-(C₉ to C₁₄ alkyl)-2-hydroxybenzaldoximes and preferred orthohydroxyarylketoimines are 5-(C₉ to C₁₄ alkyl)-2-hydroxyacetophenone oximes. Preferred dialkyl esters of an optionally substituted ethylene or polyethylene glycol are branched dialkyl esters comprising from 10 to 100 carbon atoms, wherein R⁷ or R⁸ are branched alkyl groups. Processes for the extraction of metal values from aqueous acidic and ammoniacal solutions are also provided.

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

(19) World Intellectual Property Organization
International Bureau



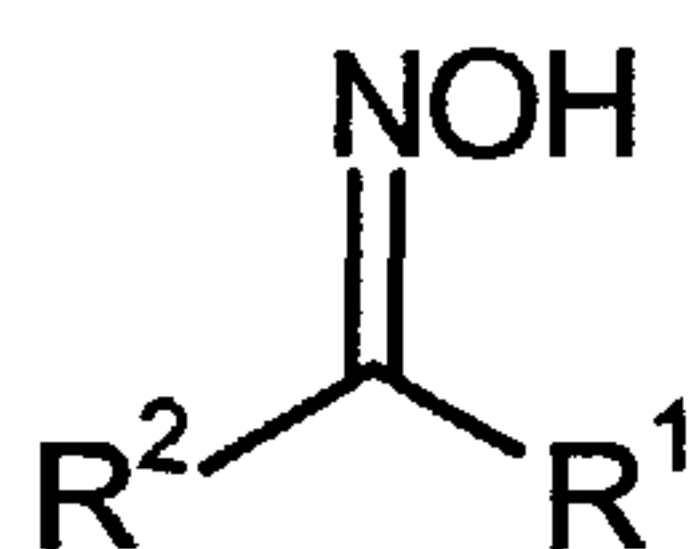
(43) International Publication Date
4 January 2001 (04.01.2001)

PCT

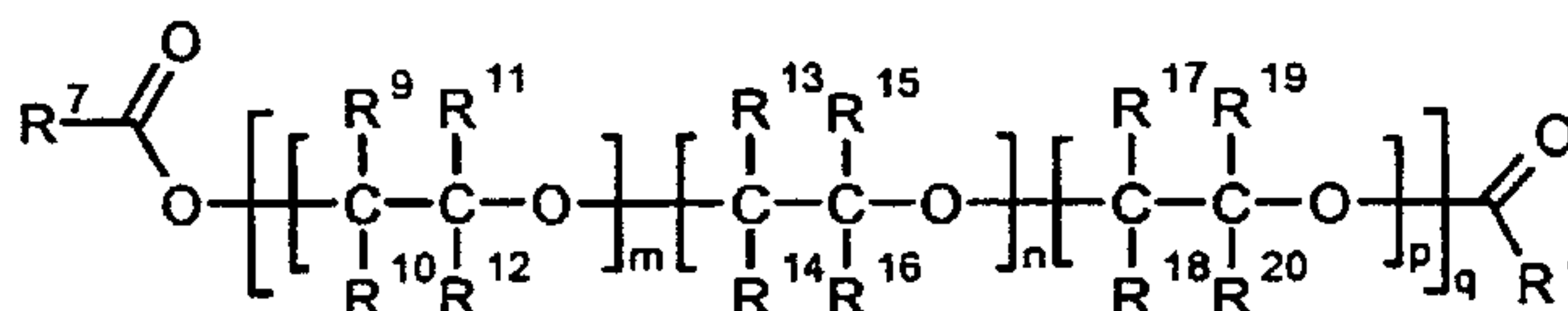
(10) International Publication Number
WO 01/00889 A1

- (51) International Patent Classification⁷: C22B 3/30, 15/00, 3/00
- (21) International Application Number: PCT/GB00/02067
- (22) International Filing Date: 30 May 2000 (30.05.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
9914669.8 24 June 1999 (24.06.1999) GB
- (71) Applicant (*for all designated States except US*): **AVECIA LIMITED** [GB/GB]; Hexagon House, Blackley, Manchester M9 8ZS (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): **CUPERTINO, Domenico, Carlo** [GB/GB]; P.O. Box 42, Hexagon House, Blackley, Manchester M9 8ZS (GB). **SUGARMAN, Alan, David** [GB/GB]; Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB).
- (74) Agents: **REVELL, Christopher et al.**; Avecia Limited, Intellectual Property Group, Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— With international search report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: COMPOSITION AND PROCESS FOR THE SOLVENT EXTRACTION OF METALS USING ALDOXIME OR KETOXIME EXTRACTANTS



(1)



(2)

(57) Abstract: A solvent extraction composition is provided which comprises one or more orthohydroxyaryldoxime or orthohydroxyarylketoimine and at least one dialkyl ester of an optionally substituted ethylene or polyethylene glycol and preferably a water immiscible organic solvent. The orthohydroxyaryldoximes, or orthohydroxyarylketoimines commonly are of Formula (1), wherein R¹ is hydrogen or a hydrocarbyl group, and R² is an ortho-hydroxyaryl group; and the dialkyl esters of an optionally substituted ethylene or polyethylene glycol commonly are of Formula (2), wherein R⁷ and R⁸ are each independently an optionally substituted alkyl group; R⁹ to R²⁰ are each independently hydrogen or optionally substituted hydrocarbyl; m, n and p are each independently 0, 1, 2, 3 or 4 provided that m+n+p is greater than or equal to 1; and q is 1, 2 or 3. Preferred orthohydroxyaryldoximes are 5-(C₉ to C₁₄ alkyl)-2-hydroxybenzaldoximes and preferred orthohydroxyarylketoimines are 5-(C₉ to C₁₄ alkyl)-2-hydroxyacetophenone oximes. Preferred dialkyl esters of an optionally substituted ethylene or polyethylene glycol are branched dialkyl esters comprising from 10 to 100 carbon atoms, wherein R⁷ or R⁸ are branched alkyl groups. Processes for the extraction of metal values from aqueous acidic and ammoniacal solutions are also provided.

COMPOSITION AND PROCESS FOR THE SOLVENT EXTRACTION OF METALS USING ALDOXIME OR KETOXIME EXTRACTANTS

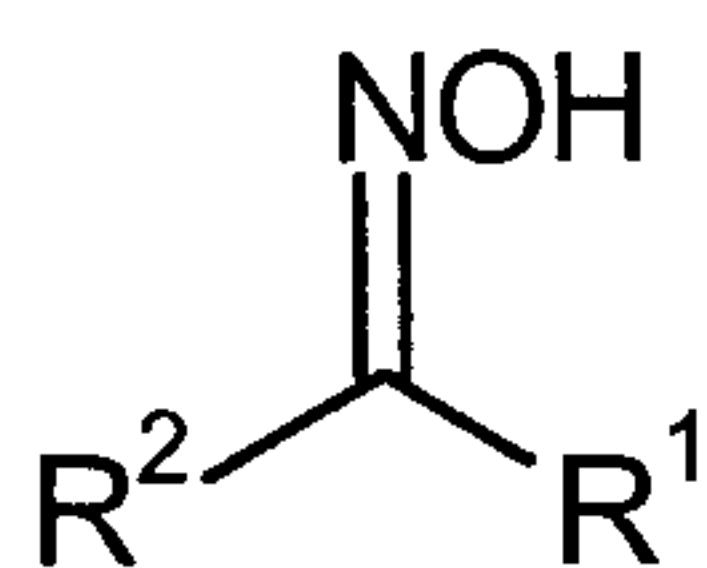
The present invention concerns a solvent extraction composition, a solvent extraction process and especially a process for the extraction of metals, particularly copper, from aqueous solutions, especially solutions obtained by leaching ores.

It is known to extract metals, especially copper, from aqueous solutions containing the metal in the form of, for example, a salt, by contacting the aqueous solution with a solution of a solvent extractant in a water immiscible organic solvent and then separating the solvent phase loaded with metal, i.e. containing at least a part of the metal in the form of a complex. The metal can then be recovered by stripping with a solution of lower pH followed for example, by electrowinning. Most commonly, the aqueous metal-containing solutions for extraction are the result of the acid leaching of ores. However it is known that some metals, especially copper, can be leached from certain ores with ammoniacal solutions. This has the advantage that solutions containing especially high concentrations of copper are derived and that there is little contamination of the solution with iron.

Solvent extractants which have found favour in recent years particularly for the recovery of copper from aqueous solutions include oxime reagents, especially o-hydroxyaryloximes and o-hydroxyarylketoximes. Whilst such reagents have been found to work well in the recovery of copper from solutions, one problem which has been encountered in the application of such reagents is that the oxime and ketoxime reagents can strongly bind metals to the extent that the efficiency of metal transfer from leach solution to strip solution can be impaired. In order to overcome such problems, modifiers have been used to effect the binding efficiency of the extractants. Typical modifiers are disclosed in WO96/25525 and in EP-A-0202833. However, as solvent extraction processes are increasingly employed in more diverse situations, there is still a need to identify further modifiers.

According to a first aspect of the present invention, there is provided a solvent extraction composition comprising one or more orthohydroxyarylaldoximes or orthohydroxyarylketoximes, and at least one dialkyl ester of an optionally substituted ethylene or polyethylene glycol. The compositions preferably also comprise a water immiscible organic solvent.

The orthohydroxyarylaldoxime or orthohydroxyarylketoxime compounds employed in the present invention are substantially water insoluble and preferably have the formula:



Formula (1)

wherein

R¹ is hydrogen or an optionally substituted hydrocarbyl group

R² is an optionally substituted ortho-hydroxyaryl group,

and salts thereof.

Whilst the invention is described herein with reference to a compound of Formula (1), it is understood that it relates to said compound in any possible tautomeric forms, and also the complexes formed between orthohydroxyaryldoximes or orthohydroxyarylketoximes and metals, particularly copper.

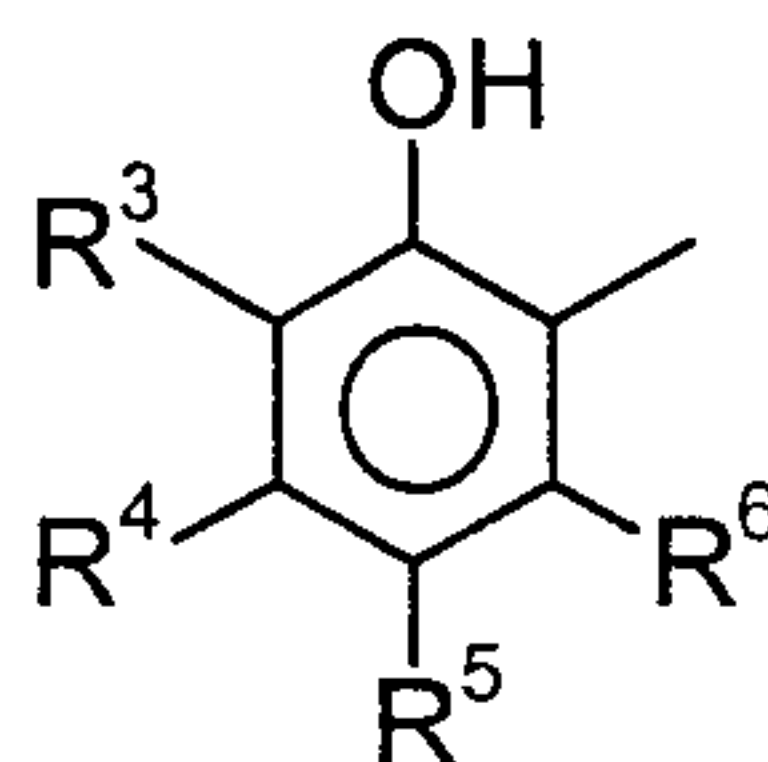
Optionally substituted hydrocarbyl groups which may be represented by R¹ preferably comprise optionally substituted alkyl and aryl groups including combinations of these, such as optionally substituted aralkyl and alkaryl groups.

Examples of optionally substituted alkyl groups which may be represented by R¹ include groups in which the alkyl moieties can contain from 1 to 20, especially from 1 to 4, carbon atoms. A preferred orthohydroxyarylketoxime is one in which R¹ is alkyl, preferably containing up to 20, and especially up to 10, and more preferably up to 3 saturated aliphatic carbon atoms, and in a most preferred orthohydroxyarylketoxime R¹ is a methyl group.

Examples of optionally substituted aryl groups which may be represented by R¹ include optionally substituted phenyl groups. When R¹ is an aryl group, it is preferably an unsubstituted phenyl group.

Most preferably R¹ represents a hydrogen atom.

Optionally substituted ortho-hydroxyaryl groups which may be represented by R² include optionally substituted phenols. Examples of optionally substituted phenols which may be represented by R² include those of formula:



wherein R³ to R⁶ each independently represent H or a C₁ to C₂₂, preferably a C₇ to C₁₅, linear or branched alkyl group. Particularly preferably only R⁵ represents a C₁₋₂₂ alkyl group, most preferably a C₇ to C₁₅ alkyl group, with R³, R⁴ and R⁶ representing H.

When R¹ or R² is substituted, the substituent(s) should be such as not to affect adversely the ability of the orthohydroxyaryldoxime or orthohydroxyarylketoxime to complex with metals, especially copper. Suitable substituents include halogen, nitro,

cyano, hydrocarbyl, such as C₁₋₂₀-alkyl, especially C₁₋₁₀-alkyl; hydrocarbyloxy, such as C₁₋₂₀-alkoxy, especially C₁₋₁₀-alkoxy; hydrocarbyloxycarbonyl, such as C₁₋₂₀-alkoxycarbonyl, especially C₁₋₁₀-alkoxycarbonyl; acyl, such as C₁₋₂₀-alkylcarbonyl and arylcarbonyl, especially C₁₋₁₀-alkylcarbonyl and phenylcarbonyl; and acyloxy, such as C₁₋₂₀-alkylcarbonyloxy and arylcarbonyloxy, especially C₁₋₁₀-alkylcarbonyloxy and phenylcarbonyloxy. There may be more than one substituent in which case the substituents may be the same or different.

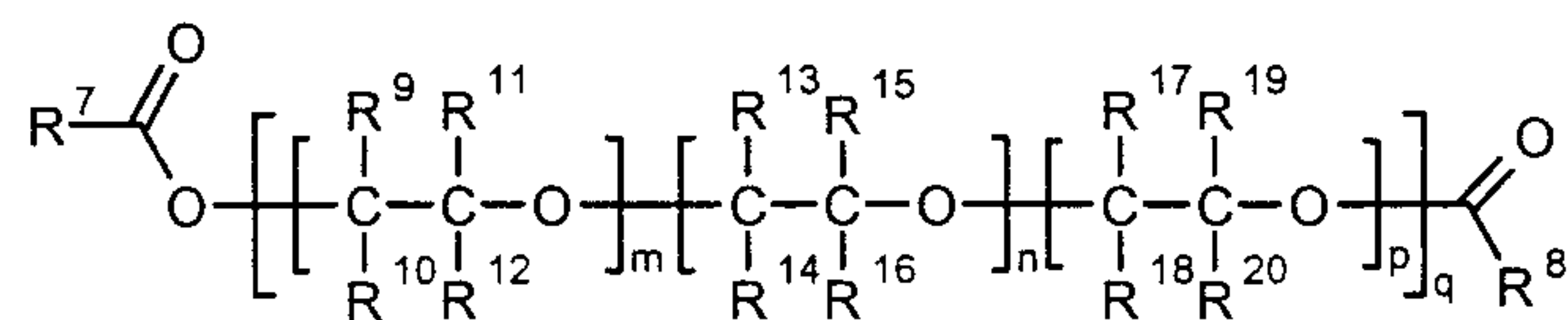
In many embodiments, when an orthohydroxyarylketoxime is employed, the orthohydroxyarylketoxime is a 5-(C₈ to C₁₄ alkyl)-2-hydroxyacetophenone oxime, particularly 5-nonyl-2-hydroxyacetophenone oxime.

In many preferred embodiments, when an orthohydroxyarylaldoxime is employed, the orthohydroxyarylaldoxime is a 5-(C₈ to C₁₄ alkyl)-2-hydroxybenzaldoxime, particularly 5-nonyl-2-hydroxybenzaldoxime.

The composition may comprise one or more different orthohydroxyarylaldoximes or orthohydroxyarylketoximes or mixtures thereof in which the nature of the substituent groups represented by R¹ and R² differ between component orthohydroxyarylaldoximes or orthohydroxyarylketoximes, especially where the component oximes are isomeric. Such isomeric mixtures may have better solubility in organic solvents than a single oxime.

The orthohydroxyarylaldoximes or orthohydroxyarylketoximes are often present in an amount of up to 60% by weight of the composition, commonly no more than 50%, and usually no more than 40 % w/w. Often, the orthohydroxyarylaldoxime or orthohydroxyarylketoxime comprises at least 1% by weight, commonly at least 2.5% by weight and usually at least 5% by weight of composition, and preferably comprises from 7.5 to 20%, more preferably 10 to 18%, such as about 15%, by weight of the composition.

The dialkyl esters of an optionally substituted ethylene or polyethylene glycol employed in the present invention are substantially water insoluble and commonly have the formula:



Formula (2)

wherein

R⁷ and R⁸ are each independently an optionally substituted alkyl group;

R⁹ to R²⁰ are each independently hydrogen or optionally substituted hydrocarbyl;

m, n and p are each independently 0, 1, 2, 3 or 4 provided that m+n+p is greater than or equal to 1; and

q is 1, 2 or 3.

The dialkyl esters of an optionally substituted ethylene or polyethylene glycol (hereinafter Esters) of the present invention often contain from 10 to 100 carbon atoms, preferably from 16 to 70 carbon atoms, such as up to 40 carbon atoms, and more preferably from 20 to 30 carbon atoms.

Optionally substituted alkyl groups which may be represented by R^7 and R^8 include groups in which the alkyl moieties often contain from 1 to 25 carbon atoms, preferably from 2 to 16 carbon atoms and especially from 4 to 12, carbon atoms. Alkyl groups which may be represented by R^7 and R^8 are preferably branched. It is especially preferred that when an alkyl group represented by R^7 and R^8 is branched, that branching be *alpha* to the carbonyl groups to which R^7 and R^8 are attached.

Optionally substituted hydrocarbyl groups which may be represented by any of R^9 to R^{20} preferably comprise optionally substituted alkyl and aryl groups including combinations of these, such as optionally substituted aralkyl and alkaryl groups.

Examples of optionally substituted alkyl groups which may be represented by R^9 to R^{20} include groups in which the alkyl moieties can contain up to 10, and especially up to 5, carbon atoms. When one of R^9 to R^{20} is an alkyl group, it is preferably an unsubstituted methyl group.

Examples of optionally substituted aryl groups which may be represented by R^9 to R^{20} include optionally substituted phenyl groups. When one of R^9 to R^{20} is an aryl group, it is preferably an unsubstituted phenyl group.

When any of R^9 to R^{20} is an optionally substituted hydrocarbyl group it is preferred that up to one of R^9 , R^{10} , R^{11} or R^{12} ; and/or up to one of R^{13} , R^{14} , R^{15} or R^{16} and/or up to one of R^{17} , R^{18} , R^{19} or R^{20} is an optionally substituted hydrocarbyl group. It is especially preferred that the optionally substituted hydrocarbyl group be an unsubstituted methyl group.

Most preferred are Esters where in each of R^9 to R^{20} are hydrogen.

The Esters optionally comprise a number of repeat units as defined by m, n, p and q. It is preferred that the total number of units as defined by the formula:

$$\text{Total Number of Units} = q(m+n+p)$$

is from 1 to 6, more preferably from 2 to 5.

In certain preferred embodiments, $n+p$ equals 0, q equals 1, m is from 2 to 4 and each of R^9 to R^{20} are hydrogen.

In certain highly preferred embodiments, $n+p$ equals 0, q equals 1, m is from 2 to 4, each of R^9 to R^{20} are hydrogen, and R^7 and R^8 are both branched C_4 to C_{12} alkyl groups.

The Esters optionally may contain other functional groups which are selected so as not to effect adversely with their function as modifiers. Functional groups which may be present include halogen, nitro, cyano, hydrocarbyl, such as C_{1-20} -alkyl, especially C_{1-10} -alkyl; hydrocarbyloxy, such as C_{1-20} -alkoxy, especially C_{1-10} -alkoxy;

hydrocarbyloxycarbonyl, such as C₁₋₂₀-alkoxycarbonyl, especially C₁₋₁₀-alkoxycarbonyl; acyl, such as C₁₋₂₀-alkylcarbonyl and arylcarbonyl, especially C₁₋₁₀-alkylcarbonyl and phenylcarbonyl; and acyloxy, such as C₁₋₂₀-alkylcarbonyloxy and arylcarbonyloxy, especially C₁₋₁₀-alkylcarbonyloxy and phenylcarbonyloxy. There may be more than one functional group in which case the functional groups may be the same or different.

Examples of useful Esters include tetraethylene glycol di-2-ethylhexanoate.

The Esters often comprise up to 30% w/w of the composition, preferably from 0.1 to 20 % w/w, and most preferably from 0.5 to 15% w/w. The weight ratio of Ester to aldoxime or ketoxime is often in the range of from 10:1 to 1:10, commonly from 5:1 to 1:5, and preferably from 1:1 to 1:4.

Organic solvents which may be used for the extraction include any mobile organic solvent, or mixture of solvents, which is immiscible with water and is inert under the extraction conditions to the other materials present. Examples of suitable solvents include aliphatic, alicyclic and aromatic hydrocarbons and mixtures of any of these as well as chlorinated hydrocarbons such as trichloroethylene, perchloroethylene, trichloroethane and chloroform. Examples of suitable hydrocarbon solvents include ESCAID 110, ESCAID 115, ESCAID 120, ESCAID 200, and ESCAID 300 commercially available from Exxon (ESCAID is a trade mark), SHELLSOL D70 and D80 commercially available from Shell (SHELLSOL is a trade mark), and CONOCO 170 commercially available from Conoco (CONOCO is a trade mark). Certain suitable solvents have a low aromatic (<1% w/w) content, for example hydrocarbon solvents such as ESCAID 110 commercially available from Exxon (ESCAID is a trade mark), and ORFOM SX 10 and ORFOM SX11 commercially available from Phillips Petroleum (ORFOM is a trade mark). Preferred solvents are hydrocarbon solvents including high flash point solvents with a high aromatic content such as SOLVESSO 150 commercially available from Exxon (SOLVESSO is a trade mark) and includes solvents which consist essentially of a mixture of trimethylbenzenes such as AROMASOL H, commercially available from Imperial Chemical Industries PLC (AROMASOL is a trade mark). Especially preferred, however, on grounds of low toxicity and wide availability are hydrocarbon solvents of relatively low aromatic content such as kerosene, for example ESCAID 100 which is a petroleum distillate with a total aromatic content of 23% commercially available from Exxon (ESCAID is a trade mark), or ORFOM SX7, commercially available from Phillips Petroleum (ORFOM is a trade mark).

In many embodiments, the composition comprises at least 30%, often at least 45% by weight, preferably from 50 to 95% w/w of water-immiscible hydrocarbon solvent.

Certain preferred compositions comprise at least one orthohydroxyaryldoxime or orthohydroxyarylketoxime which may be present in an amount up to 42% w/w, and preferably from 7.5 to 20% w/w, and at least one Ester which may also be present in an amount up to 28%, preferably from 0.5 to 15%, w/w. Compositions comprising at least

one orthohydroxyarylaldoxime or orthohydroxyarylketoxime which is present in an amount from 7.5 to 20% w/w and at least one Ester which is present in an amount of from 0.5 to 15% w/w are particularly preferred.

Particularly preferred solvent extraction compositions are those comprising from 7.5 to 20% w/w of 5-(C₈ to C₁₄ alkyl)-2-hydroxyacetophenone oxime or 5-(C₈ to C₁₄ alkyl)-2-hydroxybenzaldoxime, 0.5 to 15% w/w tetraethylene glycol di-2-ethylhexanoate, and from 65 to 92% of water-immiscible hydrocarbon solvent.

Advantageously, it may be preferred to make and supply the composition in the form of a concentrate. In certain embodiments, the concentrate may comprise only a mixture of one or more orthohydroxyarylaldoximes or orthohydroxyarylketoximes, and one or more Esters (ie no solvent is present). The concentrate may then be diluted by the addition of organic solvents as described herein above to produce compositions in the ranges as described herein above. Where the concentrate contains a solvent, it is preferred that the same solvent is used to dilute the concentrate to the "in use" concentration range. In many embodiments, the concentrate composition comprises up to 30%, often up to 20% by weight, preferably up to 10% w/w of water-immiscible hydrocarbon solvent. Often the concentrate composition comprises greater than 5% w/w of water-immiscible hydrocarbon solvent

If desired, compounds or mixtures of compounds selected from the group consisting of alkylphenols, alcohols, esters, ethers, polyethers, carbonates, ketones, nitriles, amides, carbamates, sulphoxides, and salts of amines and quaternary ammonium compounds may also be employed as modifiers in the composition of the invention. Particularly preferred are mixtures comprising a first compound selected from the group consisting of alkylphenols, alcohols, esters, ethers, polyethers, carbonates, ketones, nitriles, amides, carbamates, sulphoxides, and salts of amines and quaternary ammonium compounds and a second compound selected from the group consisting of alkanols having from 6 to 18 carbon atoms, an alkyl phenol in which the alkyl group contains from 7 to 12 carbon atoms, and tributylphosphate.

The aforementioned modifiers may be used in the preparation of extractant compositions containing one or more orthohydroxyarylaldoxime or orthohydroxyarylketoxime, at least one dialkyl ester of an optionally substituted ethylene or polyethylene glycol, one or more modifiers and a water immiscible organic solvent.

According to a second aspect of the present invention, there is provided a process for the extraction of a metal from solution in which an acidic solution containing a dissolved metal is contacted with a solvent extraction composition comprising a water immiscible organic solvent and a water-immiscible solvent extractant, whereby at least a fraction of the metal is extracted into the organic solution, characterised in that the solvent extraction composition comprises one or more orthohydroxyarylaldoxime or

orthohydroxyarylketoxime and at least one dialkyl ester of an optionally substituted ethylene or polyethylene glycol.

Metals that may be extracted in the process according to the second aspect of the present invention include copper, cobalt, nickel, manganese and zinc, most preferably copper.

The orthohydroxyarylaldoxime, orthohydroxyarylketoxime, dialkyl ester of an optionally substituted ethylene or polyethylene glycol, and water immiscible organic solvent are as herein described before. It is preferred that there is predominance of orthohydroxyarylaldoximes in relation to any orthohydroxyarylketoximes present in the solvent extraction composition. It is especially preferred that the solvent extraction composition comprises one or more orthohydroxyarylaldoximes and at least one dialkyl ester of an optionally substituted ethylene or polyethylene glycol.

The aqueous acidic solution from which metals are extracted by the process of the second aspect of the present invention often has a pH in the range of from -1 to 7, preferably from 0 to 5, and most preferably from 0.25 to 3.5. Preferably, when the metal to be extracted is copper, pH values of less than 3 chosen so that the copper is extracted essentially free from iron, cobalt or nickel. The solution can be derived from the leaching of ores or may be obtained from other sources, for example metal containing waste streams such as from copper etching baths.

The concentration of metal, particularly copper, in the aqueous acidic solution will vary widely depending for example on the source of the solution. Where the solution is derived from the leaching of ores, the metal concentration is often up to 75g/l and most often from 1 to 40g/l. Where the solution is a waste stream, the metal concentrations are often somewhat higher than those from the leaching of ores, for example up to 150g/l, usually from 75 to 130g/l.

Preferred solvent extraction compositions are aldoxime containing compositions as discussed above with respect to the first aspect of the present invention.

The process of the second aspect of the present invention can be carried out by contacting the solvent extractant composition with the aqueous acidic solution. Ambient or elevated temperatures, such as up to 75°C, can be employed if desired. Often a temperature in the range of from 5 to 60°C, and preferably from 15 to 40°C, is employed. The aqueous solution and the solvent extractant are usually agitated together to maximise the interfacial areas between the two solutions. The volume ratio of solvent extractant to aqueous solution are commonly in the range of from 20:1 to 1:20, and preferably in the range of from 5:1 to 1:5. In many embodiments, to reduce plant size and to maximise the use of solvent extractant, organic to aqueous volume ratios close to 1:1 are employed, such as 1.5:1 or less.

The mole ratio of the combined orthohydroxyarylaldoxime and orthohydroxyarylketoxime present to copper transferred is often selected to be in the

range of from 2.7:1 to 1:1. Preferably, to achieve improved hydrometallurgical properties, such as reduced viscosity and improved phase disengagement, the mole ratio of oxime to copper transferred is from 2.3:1 to 2.0:1.

After contact with the aqueous acidic solution, the metal can be recovered from the solvent extractant by contact with an aqueous acidic strip solution.

The aqueous strip solution employed in the process according to the second aspect of the present invention is usually acidic, commonly having a pH of 2 or less, and preferably a pH of 1 or less, for example, a pH in the range of from -1 to 0.5. The strip solution commonly comprises a mineral acid, particularly sulphuric acid, nitric acid or hydrochloric acid. In many embodiments, acid concentrations, particularly for sulphuric acid, in the range of from 130 to 200g/l and preferably from 150 to 180g/l are employed. When the extracted metal is copper or zinc, preferred strip solutions respectively comprise stripped or spent electrolyte from a copper or zinc electro-winning cell, typically comprising up to 80g/l copper or zinc, often greater than 20g/l copper or zinc and preferably from 30 to 70g/l copper or zinc, and up to 200g/l sulphuric acid, often greater than 120g/l sulphuric acid, and preferably from 150 to 180g/l sulphuric acid.

The volume ratio of organic solution to aqueous strip solution in the process of the second aspect of the present invention is commonly selected to be such so as to achieve transfer, per litre of strip solution, of up to 50g/l of metal, especially copper into the strip solution from the organic solution. In many industrial copper electrowinning processes transfer is often from 10g/l to 35g/l, and preferably from 15 to 20g/l of copper per litre of strip solution is transferred from the organic solution. Volume ratios of organic solution to aqueous solution of from 1:2 to 15:1 and preferably from 1:1 to 10:1, especially less than 3:1 are commonly employed.

A preferred embodiment of the second aspect of the present invention comprises a process for the extraction of a metal from aqueous acidic solution in which:

in step 1, a water-immiscible solvent extraction composition comprising an orthohydroxyaryldoxime and dialkyl ester of an optionally substituted ethylene or polyethylene glycol is first contacted with the aqueous acidic solution containing metal,

in step 2, separating the solvent extraction composition containing metal-solvent extractant complex from the aqueous acidic solution;

in step 3, contacting the solvent extraction composition containing metal-solvent extractant complex with an aqueous acidic strip solution to effect the stripping of the copper from the water immiscible phase;

in step 4, separating the metal-depleted solvent extraction composition from the loaded aqueous strip solution.

According to a third aspect of the present invention, there is provided a process for the extraction of a metal from solution in which an aqueous ammoniacal solution containing a dissolved metal is contacted with a solvent extraction composition

comprising a water immiscible organic solvent and a water-immiscible solvent extractant, whereby at least a fraction of the metal is extracted into the organic solution, characterised in that the solvent extraction composition comprises one or more orthohydroxyarylaldoxime or orthohydroxyarylketoxime and at least one dialkyl ester of an optionally substituted ethylene or polyethylene glycol.

Metals that may be extracted in the process according to the third aspect of the present invention include copper, cobalt, nickel, manganese and zinc, most preferably copper.

The orthohydroxyarylaldoxime, orthohydroxyarylketoxime, dialkyl ester of an optionally substituted ethylene or polyethylene glycol and water immiscible organic solvent are as herein described for the first aspect of the present invention. It is preferred that there is predominance of orthohydroxyarylketoximes in relation to any orthohydroxyarylaldoximes present in the solvent extraction composition. It is especially preferred that the solvent extraction composition comprises one or more orthohydroxyarylketoxime and at least one dialkyl ester of an optionally substituted ethylene or polyethylene glycol.

The aqueous ammoniacal solution from which metals are extracted by the process of the third aspect of the present invention often has a pH in the range of from 7 to 12, preferably from 8 to 11, and most preferably from 9 to 10. The solution can be derived from the leaching of ores, particularly chalcocite ores, or may be obtained from other sources, for example metal containing waste streams such as from copper etching baths.

Preferred solvent extraction compositions are those ketoxime containing compositions as discussed above with respect to the first aspect of the present invention.

The concentration of metal, particularly copper, in the aqueous ammoniacal solution will vary widely depending for example on the source of the solution. Where the solution is derived from the leaching of ores, the metal concentration is often up to 75g/l and most often from 10 to 40g/l. Where the solution is a waste stream, the metal concentrations are often somewhat higher than those from the leaching of ores, for example up to 150g/l, usually from 75 to 130g/l.

The process of the third aspect of the present invention can be carried out by contacting the solvent extractant composition with the aqueous ammoniacal solution. Ambient or elevated temperatures, such as up to 75°C can be employed if desired. Often a temperature in the range of from 15 to 60°C, and preferably from 30 to 50°C, is employed. The aqueous solution and the solvent extractant are usually agitated together to maximise the interfacial areas between the two solutions. The volume ratio of solvent extractant to aqueous solution are commonly in the range of from 20:1 to 1:20, and preferably in the range of from 5:1 to 1:5. In many embodiments, to reduce plant size

and to maximise the use of solvent extractant, organic to aqueous volume ratios close to 1:1 are employed, such as 1.5:1 or less, and preferably 1.3:1 or less.

The mole ratio of the combined orthohydroxyarylaloxime and orthohydroxyarylketoxime present to copper transferred is often selected to be in the range of from 2.7:1 to 1:1. Preferably, to achieve improved hydrometallurgical properties, such as reduced viscosity and improved phase disengagement, the mole ratio of oxime to copper transferred is from 2.3:1 to 2.0:1.

After contact with the aqueous ammoniacal solution, the metal can be recovered from the solvent extractant by contact with an aqueous strip solution having a pH lower than that from which the metal was extracted.

The aqueous lower pH strip solution employed in the process according to the third aspect of the present invention is usually acidic and is as described for the strip solution in the process of the second aspect of the present invention. When the extracted metal is copper or zinc, preferred strip solutions respectively comprise stripped or spent electrolyte from a copper or zinc electro-winning cell, typically comprising up to 80g/l copper or zinc, often greater than 20g/l copper or zinc and preferably from 30 to 50g/l copper or zinc, and up to 200g/l sulphuric acid, often greater than 120g/l sulphuric acid, and preferably from 150 to 180g/l sulphuric acid.

The volume ratio of organic solution to aqueous strip solution in the process of the third aspect of the present invention is commonly selected to be such so as to achieve transfer, per litre of strip solution, of up to 50g/l of metal, especially copper into the strip solution from the organic solution. In many industrial copper electrowinning processes transfer is often from 10g/l to 35g/l, and preferably from 15 to 20g/l of copper per litre of strip solution is transferred from the organic solution. Volume ratios of organic solution to aqueous solution of from 1:2 to 15:1 and preferably from 1:1 to 10:1, especially less than 5:1 are commonly employed.

A preferred embodiment of the third aspect of the present invention comprises a process for the extraction of a metal from aqueous ammoniacal solution in which:

in step 1, a water-immiscible solvent extraction composition comprising an orthohydroxyarylketoxime and dialkyl ester of an optionally substituted ethylene or polyethylene glycol is first contacted with the aqueous ammoniacal solution containing metal,

in step 2, separating the solvent extraction composition containing metal-solvent extractant complex from the aqueous ammoniacal solution;

in step 3, contacting the solvent extraction composition containing metal-solvent extractant complex with an aqueous strip solution of lower pH than the ammoniacal solution to effect the stripping of the copper from the water immiscible phase;

in step 4, separating the metal-depleted solvent extraction composition from the lower pH aqueous solution.

The metal can be recovered from the aqueous strip solution by conventional methods, for example by electrowinning.

The invention is further illustrated, but not limited, by the following examples.

5 Example General Methods

Each modifier was tested with the same oxime to determine the amount of modifier required to achieve a Target minimum strip level under given strip conditions. These target levels were chosen based on experience of the performance of commercial extractants under such conditions. For the three aqueous strip solutions (compositions in
10 parenthesis) the Target minimum strip levels were 1.8gpl Cu (30gpl Cu/120gpl H₂SO₄), 1.6gpl Cu (30gpl Cu/150gpl H₂SO₄) and 1.24gpl Cu (30gpl Cu/180gpl H₂SO₄). Then using the concentrations of modifier defined by the Target minimum strip level experiment, a maximum load value was determined under fixed loading conditions. Then finally by performing a strip experiment on the maximum load solutions, and calculating
15 the difference between the loaded and stripped copper values, a net copper transfer value was derived for each modifier under fixed extract and strip conditions.

Modifier Concentration required to achieve Target Minimum Strip Value:

Sample Solutions:

20 Nonylsalicylaldoxime (100g) was dissolved in the hydrocarbon solvent commercially available under the Trade name ORFOM SX7 (1l) to give a 100g/l stock solution. Then for each modifier to be tested, four separate aliquots (25ml) of the stock solution were removed and these were used to prepare the test solutions as follows:-

- 25 1) To the first aliquot (25ml) of stock solution was added 2.5g modifier and the resulting solution was then diluted to 50ml by the addition of ORFOM SX7. This gave a 50g/l oxime, 50g/l modifier test solution.
- 2) To the second aliquot (25ml) of stock solution was added 1.5g modifier and the resulting solution was then diluted to 50ml by the addition of ORFOM SX7. This gave a 50g/l oxime, 30g/l modifier test solution.
- 30 3) To the third aliquot (25ml) of stock solution was added 0.75g modifier and the resulting solution was then diluted to 50ml by the addition of ORFOM SX7. This gave a 50g/l oxime, 15g/l modifier test solution.
- 4) To the first aliquot (25ml) of stock solution no modifier was added, the solution was only diluted to 50ml by the addition of ORFOM SX7. This gave a 50g/l
35 oxime, no modifier test solution.

Evaluation procedure:

For each of the modifiers, the four test solutions were each evaluated by stripping with three copper/acid strip solutions. For this procedure, three aliquots (10ml) of each

test solution were removed separately. Each aliquot was then loaded to equilibrium with Cu^{2+} by shaking the test aliquot with an equal volume (1:1 O/A (organic/aqueous)) of an aqueous CuSO_4 solution comprising 10g/l Cu^{2+} buffered at pH4.5 for two minutes in a separating funnel, discarding the aqueous phase and repeating with fresh copper solution three further times. Once loaded with copper, each organic phase was isolated and then stripped of copper. Stripping of each solution was carried out by shaking the test aliquot with an equal volume of a given strip solution for two minutes in a separating funnel, discarding the aqueous phase and repeating with fresh strip solution three further times. Aqueous strip solutions consisting of 30gpl Cu/120gpl H_2SO_4 , 30gpl Cu/150gpl H_2SO_4 and 30gpl Cu/180gpl H_2SO_4 were used for these evaluations. The copper concentration of the resulting organic phases were determined by atomic absorption spectroscopy. In total twelve measurements were made for each modifier tested.

The data gathered for each of the strip solutions employed was plotted to give a curve showing copper left in the organic phase post stripping versus concentration of modifier required. This was then used to determine the required amount of each modifier to achieve the target minimum strip level under each of the stripping conditions.

Net Copper Transfer:

Test Solutions:

Three test solutions were prepared for each modifier containing 50g/l oxime and modifier at the concentration determined to achieve the Target minimum strip values. These were prepared from aliquots (25ml) of stock solution (nonylsalicylaldoxime (100g) dissolved in ORFOM SX7 (1l) to give a 100g/l stock solution) and by adding the required amount of modifier then diluting to 50ml by the addition of ORFOM SX7.

Evaluation Procedure:

Maximum Load Value:

Aliquots (10ml) of each test solution were removed separately and each loaded to equilibrium with copper by contacting with an aqueous CuSO_4 solution comprising 5g/l Cu^{2+} at 1:1 O/A by shaking 4 times for 2min in a separating funnel with fresh loading solution. Copper loading solutions of pH 1.0, 1.5 and 2.0 were used in the evaluation. Five loaded organic solutions were prepared for each modifier, one at pH 1.0, one at pH 1.5 and three at pH 2.0. The organic layers were separated and filtered through phase separation media before being analysed for copper content by atomic absorption spectroscopy.

Strip Value:

The three organic solutions for each modifier loaded at pH 2.0 were then stripped, a different strip condition being used for each. Stripping was carried out at 1:1 O/A by

contacting an aliquot (5ml) of the loaded organic solution with aqueous strip solutions comprising 30gpl Cu/120gpl H₂SO₄, 30gpl Cu/150gpl H₂SO₄ or 30gpl Cu/180gpl H₂SO₄ (contact was by shaking 4 times for 2min in a separating funnel with fresh strip solution). Copper stripping was determined by measuring copper levels in the organic phase by atomic absorption spectroscopy.

As the minimum stripping that can be achieved by the strip conditions is independent of the load conditions, the net copper transfer for a combination of load and strip conditions was determined for each modifier/oxime composition by subtracting the Strip Value for a given strip solution from the Load Value at a given pH.

Example 1

The following results were obtained for the Ester, tetraethyleneglycol di-2-ethylhexanoate.

The levels of modifier required to achieve the target minimum strip values were 27gpl (30/180), 34gpl (30/150) and 41gpl (30/120).

Using these modifier concentrations a matrix of net copper transfer values under the given pH loading conditions and the strip conditions were generated and are shown in Table 1.

gpl modifier	pH1 - 30/120	pH1 - 30/150	pH1 - 30/180	pH1.5 - 30/120	pH1.5 - 30/150	pH1.5 - 30/180	pH2 - 30/120	pH2 - 30/150	pH2 - 30/180
27	2.945	3.44	3.865	3.615	4.11	4.535	3.765	4.26	4.685
34	3.095	3.625	4.02	3.845	4.375	4.77	4.025	4.555	4.95
41	3.2	3.715	4.03	4.08	4.595	4.91	4.16	4.675	4.99

Table 1

Comparative Example A

The following results were obtained for a known modifier 2,2,4-trimethyl-1,3-pentanediol di-isobutyrate.

The levels of modifier required to achieve the target minimum strip values were 41gpl (30/180), 48gpl (30/150) and 55gpl (30/120).

Using these modifier concentrations a matrix of net copper transfer values under the given pH loading conditions and the strip conditions were generated and are shown in Table 2.

gpl modifier	pH1 - 30/120	pH1- 30/150	pH1- 30/180	pH1.5 - 30/120	pH1.5 - 30/150	pH1.5 - 30/180	pH2 - 30/120	pH2 - 30/150	pH2 - 30/180
41	2.71	3.26	3.66	3.53	4.08	4.48	3.65	4.2	4.6
48	2.925	3.425	3.725	3.675	4.17	4.475	3.85	4.35	4.65
55	3.08	3.58	3.88	3.85	4.35	4.65	4	4.5	4.8

Table 2

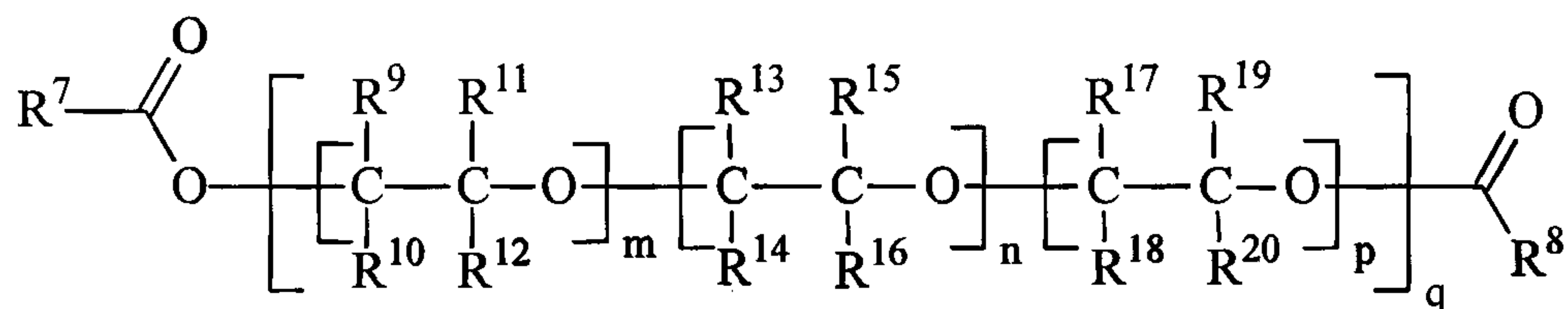
The results show that less tetraethyleneglycol di-2-ethylhexanoate (a modifier according to the present invention) is required to achieve the minimum strip value than the known modifier. Furthermore, a point by point comparison of the data presented for each modifier, shows that under each set of load/strip conditions, not only is less Ester modifier required, a higher net copper transfer is achieved and hence the composition of the present invention is a more effective copper transfer agent than the composition employing the known modifier.

75365-236

15

CLAIMS:

1. A solvent extraction composition comprising one or more orthohydroxyarylaloximes or orthohydroxyarylketoximes, and at least one dialkyl ester of an optionally substituted ethylene or polyethylene glycol selected from the class of compounds represented by formula:



Formula (2)

wherein

- 10 R⁷ and R⁸ are each independently an optionally substituted alkyl group;

R⁹ to R²⁰ are each independently hydrogen or optionally substituted hydrocarbyl;

- 15 m, n and p are each independently 0, 1, 2, 3 or 4 provided that m+n+p is greater than or equal to 1; and

q is 1, 2 or 3.

2. A composition according to claim 1, wherein n+p equals 0, q equals 1, m is from 2 to 4 and each of R⁹ to R²⁰ are hydrogen.

- 20 3. A composition according to claim 1 or 2, wherein one or both of R⁷ or R⁸ is a branched alkyl group.

4. A composition according to any one of claims 1 to 3, wherein n+p equals 0, q equals 1, m is from 2 to 4, each of R⁹ to R²⁰ are hydrogen, and R⁷ and R⁸ are both
25 branched C₄ to C₁₂ alkyl groups.

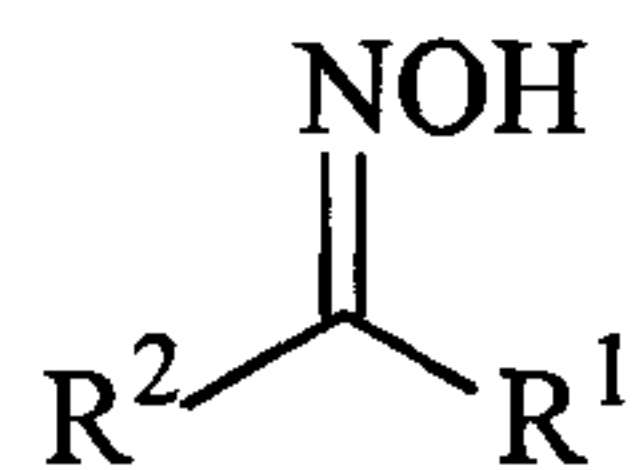
75365-236

16

5. A composition according to any one of claims 1 to 4, wherein the dialkyl ester of an optionally substituted ethylene or polyethylene glycol comprises an ester comprising from 10 to 56 carbon atoms.

5 6. A composition according to any one of claims 1 to 5, wherein the dialkyl ester of an optionally substituted polyethylene glycol is tetraethyleneglycol di-2-ethylhexanoate.

7. A composition according to any one of claims 1 to 6, wherein the orthohydroxyarylaldoxime or
10 orthohydroxyarylketoxime is selected from the class of compounds represented by the Formula (1),



Formula (1)

15 wherein

R^1 is hydrogen or an optionally substituted hydrocarbyl group

R^2 is an optionally substituted ortho-hydroxyaryl group,

20 and salts thereof.

8. A composition according to any one of claims 1 to 7, wherein the orthohydroxyarylketoxime is a 5-(C₉ to C₁₄ alkyl)-2-hydroxyacetophenone oxime.

9. A composition according to any one of claims 1 to 7, wherein the orthohydroxyarylketoxime is a 5-nonyl-2-hydroxy-acetophenone oxime.

25

75365-236

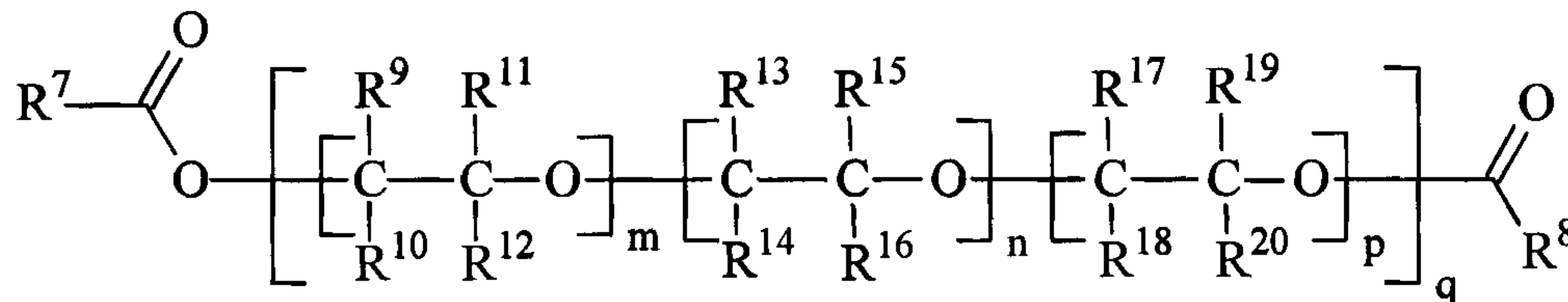
17

10. A composition according to any one of claims 1 to 9, wherein the orthohydroxyarylaloxime is a 5-(C₉ to C₁₄ alkyl)-2-hydroxybenzaloxime.

11. A composition according to any one of claims 1 to 9, wherein the orthohydroxyarylaloxime is a 5-nonyl-2-hydroxy-benzaloxime.

12. A composition according to any one of claims 1 to 11, further comprising a water immiscible organic solvent.

13. A process for the extraction of a metal from solution in which either an acidic solution containing a dissolved metal or an aqueous ammoniacal solution containing a dissolved metal is contacted with a solvent extraction composition comprising a water immiscible organic solvent and a water-immiscible solvent extractant, whereby at least a fraction of the metal is extracted into the organic solution, characterised in that the solvent extraction composition comprises one or more orthohydroxyarylaloxime or orthohydroxyarylketoxime and at least one dialkyl ester of an optionally substituted ethylene or polyethylene glycol selected from the class of compounds represented by formula:



Formula (2)

wherein

R⁷ and R⁸ are each independently an optionally substituted alkyl group;

75365-236

18

R^9 to R^{20} are each independently hydrogen or optionally substituted hydrocarbyl;

m, n and p are each independently 0, 1, 2, 3 or 4 provided that $m+n+p$ is greater than or equal to 1; and

5 q is 1, 2 or 3.

14. A process according to claim 13, wherein $n+p$ equals 0, q equals 1, m is from 2 to 4 and each of R^9 to R^{20} are hydrogen.

15. A process according to claim 13 or 14, wherein one
10 or both of R^7 or R^8 is a branched alkyl group.

16. A process according to any one of claims 13 to 15, wherein $n+p$ equals 0, q equals 1, m is from 2 to 4, each of R^9 to R^{20} are hydrogen, and R^7 and R^8 are both branched C_4 to C_{12} alkyl groups.

15 17. A process according to any one of claims 13 to 16, wherein the dialkyl ester of an optionally substituted ethylene or polyethylene glycol comprises an ester comprising from 10 to 56 carbon atoms.

18. A process according to any one of claims 13 to 17,
20 wherein there is a predominance of orthohydroxyarylaloximes in relation to any orthohydroxyarylketoximes present in the solvent extraction composition.

19. A process according to any one of claims 13 to 17,
wherein there is a predominance of orthohydroxyarylketoximes
25 in relation to any orthohydroxyarylaloximes present in the solvent extraction composition.

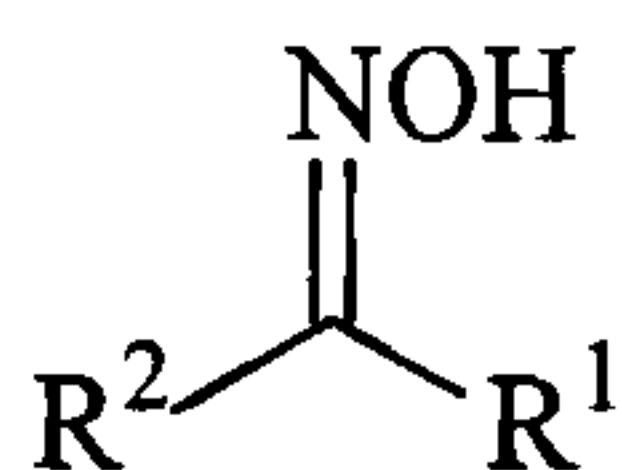
20. A process according to any one of claims 13 to 19, wherein the metal is copper, zinc, cobalt or nickel.

75365-236

19

21. A process according to claim 20, wherein the metal is copper.

22. A process according to any one of claims 13 to 21, wherein the orthohydroxyarylaldoxime or
5 orthohydroxyarylketoxime is selected from the class of compounds represented by the Formula (1),



Formula (1)

wherein

10 R^1 is hydrogen or an optionally substituted hydrocarbyl group

R^2 is an optionally substituted ortho-hydroxyaryl group,

and salts thereof.

15 23. A process according to any one of claims 13 to 22, wherein the orthohydroxyarylketoxime is a 5-(C₉ to C₁₄ alkyl)-2-hydroxyacetophenone oxime.

24. A process according to any one of claims 13 to 22, wherein the orthohydroxyarylketoxime is a 5-nonyl-2-hydroxy-
20 acetophenone oxime.

25. A process according to any one of claims 13 to 24, wherein the orthohydroxyarylaldoxime is a 5-(C₉ to C₁₄ alkyl)-2-hydroxybenzaldoxime.

26. A process according to any one of claims 13 to 24, wherein the orthohydroxyarylaldoxime is a 5-nonyl-2-hydroxy-
25 benzaldoxime.

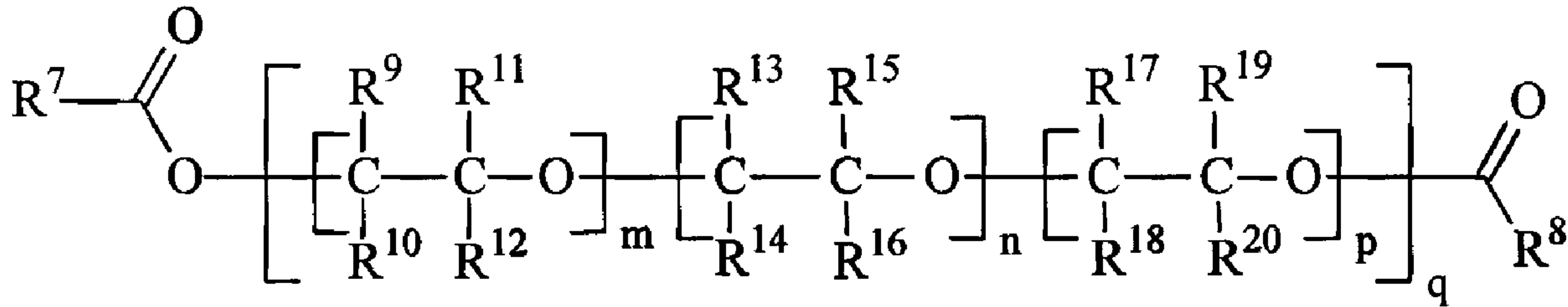
75365-236

20

27. A process according to any one of claims 13 to 26, wherein the dialkyl ester of an optionally substituted polyethylene glycol is tetraethyleneglycol di-2-ethylhexanoate.

SMART & BIGGAR
OTTAWA, CANADA

PATENT AGENTS



Formula (2)