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(54) **Process for the disposal of chlorinated organic products by oxidation treatment.**

(57) A process for the disposal of chlorinated organic products, wherein said products are treated with a H_2O_2 aqueous solution in the presence of Fe(II) ions, optionally in association with other transition metal ions selected from Cu(II), Ti(IV), Mn(II), Co(II), Ni(II), W(IV) and Mo(IV), or mixtures thereof, and in the presence of a phase transfer agent. The process leads to a substantially complete oxidation of the chlorinated organic product, with formation of non-toxic substances and good mineralization degree of chlorine atoms.

EP 0 593 895 A1

The present invention relates to a process for the disposal of chlorinated organic products. More particularly, the present invention relates to a process for the disposal of chlorinated organic products by an oxidation treatment with hydrogen peroxide (H_2O_2), in the presence of Fe(II) ions, optionally associated with other transition metal ions, and of a phase transfer agent.

The chlorinated organic products are a class of substances widely used in various technological fields. Among them, the compounds having alkyl, aromatic, or alkylaromatic structure, such as polychlorobiphenyls (PCBs), 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT), tetrachloroethane, dichlorobenzenes, chlorophenols, hexachlorocyclohexane, or olefinic structure, such as trichloroethylene, are the more common.

Generally, they are toxic and highly polluting products, whose disposal after use involves many problems. In fact, it is necessary to utilize a disposal process, applicable also on a large scale, which is as much as possible efficacious, economical and free from risks for the environment. It is particularly difficult to reach said optimum objective, since the chlorinated organic products have a high stability and, when treated with chemical and/or physical means, form highly polluting by-products.

For instance, polychlorobiphenyls (PCBs) are highly toxic and cancerogenous chloroaromatic compounds, which were broadly utilized since short ago, thanks to their dielectric properties, as oils for electrical equipment, and in particular for capacitors. Owing to their high toxicity, the regulations in force impose the PCBs elimination and their substitution with hydrocarbon mineral oils. That makes necessary to remove great amounts of PCBs, which usually are either dissolved in organic solvents (for example hexachlorobenzene), or impregnated in isolating and/or supporting materials, such as paper, paper-board, wood, etc. Furthermore, it is often necessary to remove the PCBs from mineral oils, which could be contaminated in consequence of a not correct cleaning of the electrical equipment before the replacement.

The most commonly utilized treatment for the disposal of chlorinated organic products is burning, which is carried out in properly equipped plants in order to prevent the formation of utmost toxic chloro-organic compounds, such as parachlorodibenzodioxines, parachlorodibenzofurans and the like. In any event, this is an expensive process, not free from risks for the environment, apart from the fact that it involves the elimination not only of the chlorinated compounds, but also of the materials polluted by them.

The Applicant has now found a process for the disposal of chlorinated organic products, which comprises oxidating such products with H_2O_2 in the presence of suitable catalysts and phase transfer agents, with formation of non-toxic substances and possibility of recovering the polluted material, with considerable economical and environmental advantages in comparison with the processes utilized so far.

Therefore, an object of the present invention is a process for the disposal of chlorinated organic products, which comprises treating said products with a H_2O_2 aqueous solution, in the presence of Fe(II) ions, optionally in association with one or more transition metal ions selected from Cu(II), Ti(IV), Mn(II), Co-(II), Ni(II), W(IV) and Mo(IV), and in the presence of a phase transfer agent.

Among the chlorinated products to which the process of the present invention can be applied we can mention for exemplifying purposes those having:

(a) an aromatic structure, such as polychlorobiphenyls (PCBs), chlorobenzenes (for instance, ortho- and methadichlorobenzene), chlorophenols (for instance para-, tri- and penta-chlorophenol), etc.;

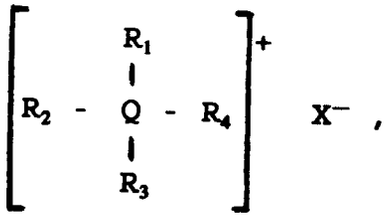
(b) an alkylaromatic structure, such as 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT), and others;

(c) an olefinic structure, such as trichloroethylene, perchlorobutadiene, etc.;

(d) an aliphatic or cycloaliphatic structure, such as tetrachloroethane, hexachlorocyclohexane, hydrated chloral, hexachloroethane, perchloroacetone, etc.

The reaction involved in the process of the present invention is an oxidation reaction in heterogeneous phase, as the chlorinated organic products are insoluble in the aqueous phase containing the H_2O_2/Fe^{2+} oxidizing system. Necessary is therefore the presence of a phase transfer agent, i.e. of a product which acts as a "bridge" between the molecules of the chlorinated organic product and the oxidizing system. For an exhaustive discussion of such products see C. Starks, C. Liotta, "Phase transfer catalysts", Academic Press (1978).

Among the products known in the art as phase transfer agents, the ones which are advantageously utilizable in the process of the present invention are the ammonium, phosphonium or arsonium salts of general formula:



wherein:

Q is selected from N, P and As;

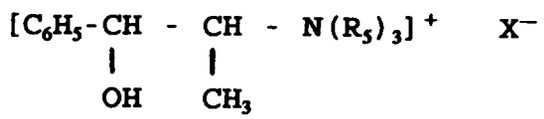
R_1, R_2, R_3 and R_4, like or different from one another, are selected from hydrogen, C_1-C_{35}, preferably C_1-C_{12}, alkyl groups, C_6-C_{10} aryl groups, C_7-C_{30}, preferably C_7-C_{12}, arylalkyl or alkylaryl groups, on condition that at least one out of R_1, R_2, R_3 and R_4 is different from hydrogen;

X^- is selected from OH^-, Cl^-, Br^-, I^- and BH_4^-.

Another class of phase transfer agents utilizable in the process of the present invention is represented by the pyridinium salts of formula:

wherein R is a C_1-C_{20} alkyl group, while X^- is the same as defined above.

A further class of products utilizable as phase transfer agents in the process of the present invention is the one of ephedrine salts having the formula:



wherein:

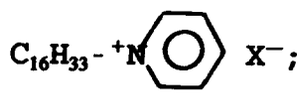
R_5, like or different from each other, are C_1-C_6 alkyl groups;

X^- is the same as defined above. Such products are described by Gani V., Tapinte C., Viout P. in "Tetrahedron Letters", p. 4435, 1983, and by Bunton C., Robinson L., Stam M. in "Tetrahedron Letters", p. 121, 1971.

It is also possible to utilize mixtures of different phase transfer agents, so as to combine in the best way the characteristics of each type of transfer agent, in order to obtain a good mineralization of the chlorine atoms as well as a complete elimination of the chlorinated organic products.

Examples of phase transfer agents utilizable in the process of the present invention are:

$(C_4H_9)_4N^+ X^-$; $(C_{10}H_{21})_3N^+C_3H_7 X^-$; $(C_{18}H_{37})_3N^+CH_3 X^-$; $(C_{18}H_{37})_2N^+(CH_3)_2 X^-$; $(C_4H_9)_3P^+C_{16}H_{33} X^-$; $(C_7H_{15})_3N^+CH_3 X^-$; $(C_6H_5)_3As^+CH_3 X^-$; $(C_6H_5CH_2)N^+(CH_3)_3 X^-$;



etc.

Particularly preferred for the embodiment of the present invention are the tetraalkylammonium salts, in which the alkyls, like or different from one another, have 1 to 35 carbon atoms, preferably 1 to 12 carbon atoms.

Usually, the chlorinated organic products to be removed are present in amounts ranging from 100 to 5,000 ppm, while the phase transfer agent is utilized in concentrations, referred to the aqueous phase, ranging from 20 to 500 ppm, preferably from 100 to 300 ppm.

Besides the phase transfer agents, the process of the present invention comprises the use of Fe(II) ions as catalysts, optionally associated with one or more transition metal ions selected, from Cu(II), Ti(IV), Mn(II), Co(II), Ni(II), W(IV) and Mo(IV). Among them, Cu(II) ions are preferred. Metal ions are added in amounts usually ranging from 50 to 1,000 ppm for the Fe(II) ions and from 0 to 400 ppm for the other transition metal ions indicated above. In a preferred embodiment, mixtures of Fe(II) ions and Cu(II), Ti(IV), Mn(II), Co-(II), Ni(II), W(IV), or Mo(IV) ions are utilized in equimolar amounts, each of them in concentrations ranging from 50 to 400 ppm, preferably from 150 to 250 ppm.

The above mentioned metal ions are added in the form of soluble salts. In particular, as to Fe(II) ions, it is possible to use for instance: ferrous sulphate, ferrous chloride, ferrous nitrate, ammonium ferrous sulphate, etc. Heptahydrate ferrous sulphate $FeSO_4 \cdot 7H_2O$ is preferred from the operative and economic viewpoint. Among the Cu(II) salts, for instance pentahydrate cupric sulphate $CuSO_4 \cdot 5H_2O$ can be used.

As regards hydrogen peroxide, it is utilized in the form of an aqueous solution, in such amounts that the molar ratio of added H_2O_2 to initially present chlorinated product generally ranges from 0.2 to 100, preferably from 0.2 to 30. The concentration of the hydrogen peroxide aqueous solution is not a discriminating parameter; to simplify the operative modalities, hydrogen peroxide solutions at 30-50% by volume are generally used. The hydrogen peroxide solution is preferably added gradually and continuously to the reaction mixture in order to more easily control the reaction conditions, in particular temperature and pH. The addition rate usually ranges from 0.2 to 3 ml/min, but it can be varied over a wider range, depending on the specific reaction conditions.

The reaction temperature can vary over a wide range, generally from 40 ° to 200 °C, preferably from 70 ° to 120 °C. The pH generally ranges from 2 to 7, approximately, preferably from 3 to 4, approximately, and it is maintained in such ranges during the reaction by adding little amounts of a aqueous solution of an acid (for example H_2SO_4) or of a base (for example NaOH).

The process of the present invention leads to a quantitative conversion of the chlorinated organic product into non-toxic products, accompanied with a good mineralization level of the chlorine atoms, i.e. conversion of the organic chlorine into chlorine ions.

In the case the chlorinated product to be disposed is dissolved in an organic solvent or in a mineral oil of hydrocarbon type, the reaction mixture is heated to the prefixed reaction temperature and then it is intensely stirred in order to bring the two phases into intimate contact, thereby obtaining a water/oil macroemulsion (the predominant phase being the organic phase).

The present invention is illustrated more in detail by the following examples, which are given merely to illustrate and not to limit the scope of the invention.

In each example, the reaction trend was followed by withdrawing, after programmed additions of hydrogen peroxide, little amounts of the reaction mixture and by determining the following parameters thereof:

(a) Concentration of the chlorinated organic product.

It is determined by gas chromatographic analysis (2-meter packed column with fixed phase Tenax(R); carrying gas: nitrogen; temperature program: isotherm at 100 °C for 2 minutes; gradient at 10 °C/min. up to 180 °C; isotherm at 180 °C for 25 minutes). Each injection (0.6 µl) is carried out with a sample diluted with CH_2Cl_2 in a 1:1 ratio, to which CH_3OH is added as an internal standard.

As regards PCBs, all the calculations have been referred to the three main PCBs isomers, for which the following composition has been determined:

$C_{12}H_7Cl_3$	21.21%
$C_{12}H_5Cl_5$	0.95%
$C_{12}H_6Cl_4$	77.83%

On the basis of such composition, an average molecular weight of 280.5 has been determined, the average number of chlorine atoms being equal to 3.74.

(b) Chlorine ion concentration.

The chlorine ions are recovered by means of extraction with H_2O acidified with 0.1% of HNO_3 and are analyzed through voltimetric titration in an acid medium with $AgNO_3$.

(c) COD (Chemical Oxygen Demand).

It is determined by oxidation with potassium bichromate in acid medium and titration with ferrous sulphate, according to the method described by N.W.Hanson in "Official, Standardized and Recommended Methods of Analysis" (page 383, The Society for Analytical Chemistry, 1973).

EXAMPLES 1-3

455 ml of a mineral oil contaminated with PCBs (3431 ppm) were introduced into a reaction flask equipped with condenser, dropping funnels, pH-meter and magnetic stirrer. Then it was added an aqueous solution consisting of 45 ml of H_2O, in which there were dissolved: $FeSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ in such amounts as to obtain a concentration of 200 ppm for both the Fe^{2+} ions and the Cu^{2+} ions; tetrabutylammonium hydroxide (ITBA) in amounts equal to:

- 150 ppm (Example 1);
- 300 ppm (Example 2);
- 0 ppm (Example 3, comparative).

The resulting mixture was heated in an oil bath to 95 °C and the pH was adjusted by means of small additions of a 10% NaOH aqueous solution or of a 15% H_2SO_4 aqueous solutions until a value of about 3.0 was obtained. The mixture was intensely stirred in order to form a water-in-oil macroemulsion. Then, a H_2O_2 aqueous solution (45% by volume) was gradually added at a rate of about 0.6 ml/min. After programmed additions of hydrogen peroxide (as indicated in Table I), reaction mixture samples (5 ml each) were drawn for the analysis. For each sample, the residual PCBs concentration ([PCBs]) and the chlorine ion concentration ($[Cl^-]$) were determined according to the above described modalities. The results are reported in Table I, where also the mineralization per cent (%$[Cl^-]$) is indicated, expressed as ratio between the actually obtained Cl^- ion concentration and the maximum obtainable Cl^- ion concentration.

During the reaction, the pH was maintained around 3.0 by means of small additions (0.1-0.3 ml) of the NaOH or H_2SO_4 solutions, while the temperature was maintained constant at 94 °C.

The reaction with 150 ppm of ITBA (Example 1) and the one without ITBA (Example 3) lasted 60 minutes, while the reaction with 300 ppm of ITBA (Example 2) lasted 95 minutes.

From a comparison between the obtained data, it is inferable, firts of all, that, without the aid of the phase transfer agent, no PCBs oxidation occurs. With the addition of the phase transfer agent, an almost complete PCBs elimination is obtained, with a satisfactory mineralization degree, in particular in the case of the reaction with a low ITBA concentration (Example 1).

EXAMPLES 4-6

Following the same modalities described for Examples 1-3, the effectiveness of another phase transfer agent, tetrabutylammonium bromide (TBAB), was checked by comparing the following reactions:

- with 150 ppm of TBAB (Example 4);
- with 472 ppm of TBAB (Example 5);
- without TBAB (Example 6, comparative).

The data obtained are indicated in Table II. As for Examples 1-3, it is possible to observe that without phase transfer agent the reaction does not occur and that the best results, in terms of PCBs oxidation as well as of PCBs mineralization, are obtained with low concentrations of transfer agent (Example 4).

EXAMPLES 7-9

Following the same modalities described for Examples 1-3, the effectiveness of another phase transfer agent, tetrabutylammonium iodide (TBAI), was checked by comparing the following reactions:

- with 166 ppm of TBAI (Example 7);
- with 460 ppm of TBAI (Example 8);
- without TBAB (Example 9, comparative).

The data obtained are indicated in Table III.

EXAMPLES 10-11

Following the same modalities described for Examples 1-3, the effectiveness of a phase transfer agent mixture (ITBA + TBAB) was checked by comparing the following reactions:

- with 100 ppm of ITBA + 100 ppm of TBAB (Example 10);
- without phase transfer agents (Example 11, comparative).

The data obtained are indicated in Table IV.

From a comparison of the results of Example 10 with the ones obtained in Examples 1, 4 and 7, it is evident that the coupling of the two phase transfer agents of Example 10 permits to best combine a substantially quantitative PCBs oxidation with a good PCBs mineralization degree.

EXAMPLE 12

The same reactor utilized for the preceding examples was filled with 500 ml of H_2O, in which the following products were dissolved: $FeSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ in such amounts as to obtain a 200 ppm concentration for both Fe^{3+} and Cu^{2+} ions; tetrabutylammonium hydroxide (ITBA) in an amount equal to 150 ppm.

20 g of PCBs-contamined paper, which had been previously cut into little pieces, were then introduced into the reactor. The PCBs concentration in the paper was equal to 1060 ppm. It was determined on a paper sample (1 g) by means of continuous extraction at room temperature for 14 hours with 20 ml of CH_2Cl_2; the PCBs-containing solvent was then analyzed via gas chromatography using methanol as internal standard.

Maintaining the solution under intense stirring, a 45% hydrogen peroxide aqueous solution was gradually added until a total H_2O_2 concentration equal to 127.5 g/l was obtained. On conclusion of the reaction, the chloride ion concentration was determined in the aqueous phase through voltimetric titration in an acid medium with $AgNO_3$. The residual PCBs concentration both in the aqueous phase and in the paper pulp was determined via gas chromatography after extraction with CH_2Cl_2, as described hereinabove. The data obtained are indicated in Table V.

EXAMPLE 13 (oxidation of hexachlorocyclohexane)

0.5 g of hexachlorocyclohexane (ECE) were introduced into a 250 ml round-bottomed reaction flask equipped with dropping funnels, pH-meter and magnetic stirrer. Thereafter, an aqueous solution was added consisting of 100 ml of H_2O, in which: $FeSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ in such amounts to obtain a concentration equal to 200 ppm for both Fe^{2+} and Cu^{2+} ions; tetrabutylammonium hydroxide (ITBA) in amounts equal to 500 ppm, had been dissolved.

The resulting mixture was heated in an oil bath to 95 °C; the pH was adjusted at a value of about 3.4-3.5 by means of small additions of a 15% H_2SO_4 aqueous solution or of a 10% NaOH aqueous solution. The mixture was intensely stirred in order to dissolve all ECE. Then, a H_2O_2 aqueous solution (56% by volume) was gradually added at a rate of about 0.4 ml/min. After programmed additions of H_2O_2 (as indicated in Table VI), reaction mixture samples (5 ml each) were drawn for analysis. In Table VI, the added amounts of H_2O_2 are expressed as number of stoichiometric equivalents; by stoichiometric equivalent is meant the theoretic amount of H_2O_2 (100%) necessary for the complete oxidation of the organic substances to CO_2 and H_2O.

For each sample, the residual ECE concentration ([ECE]), the COD and the chlorine ion concentration (-[Cl^-]) were determined according to the above described modalities. The results are reported in Table VI, where also the mineralization per cent (%[Cl^-]) is indicated, expressed as ratio between the actually obtained Cl^- ion concentration and the maximum obtainable Cl^- ion concentration.

During the reaction, the pH was maintained around 3.4 by means of small additions (0.1-0.2 ml) of the NaOH or H_2SO_4 solutions, while the temperature was maintained constant at 97 °C.

EXAMPLE 14 (oxidation of metha-chlorobenzene)

1 g (0.766 ml) of metha-dichlorobenzene (MDB) was introduced into a 500 ml round-bottomed reaction flask equipped with dropping funnels, pH-meter and magnetic stirrer. Thereafter, an aqueous solution was added consisting of 200 ml of H_2O, in which: $FeSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ in such amounts to obtain a concentration equal to 200 ppm for both Fe^{2+} and Cu^{2+} ions; tetrabutylammonium hydroxide (ITBA) in amounts equal to 500 ppm, had been dissolved.

The resulting mixture was heated in an oil bath to 95 °C; the pH was adjusted at a value of about 3.5 by means of small additions of a 15% H_2SO_4 aqueous solution or of a 10% NaOH aqueous solution. The mixture was intensely stirred in order to dissolve all MDB. Then, a H_2O_2 aqueous solution (60% by volume) was gradually added at a rate of about 0.44 ml/min. After programmed additions of H_2O_2 (as indicated in Table VI), reaction mixture samples (20 ml each) were drawn for analysis. For each sample, the residual MDB concentration ([MDB]) and the chlorine ion concentration ([Cl^-]) were determined according to the above described modalities. The results are reported in Table VI, where also the mineralization per cent (%[Cl^-]) is indicated, expressed as ratio between the actually obtained Cl^- ion concentration and the maximum obtainable Cl^- ion concentration.

During the reaction, the pH was maintained around 3.5 by means of small additions (0.1-0.2 ml) of the NaOH or H_2SO_4 solutions, while the temperature was maintained constant at 97 °C.

EXAMPLES 15-17 (oxidation of chlorophenols)

6.25 g of para-chlorophenol (PCF) (Example 15), or 0.25 g of trichlorophenol (TCF) (Example 16), or 0.25 g of pentachlorophenol (PECF) (Example 17), were introduced into a 500 ml round-bottomed reaction flask equipped with dropping funnels, pH-meter and magnetic stirrer. Thereafter, an aqueous solution was added consisting of 250 ml of H_2O, in which: $FeSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ in such amounts to obtain a concentration equal to 200 ppm for both Fe^{2+} and Cu^{2+} ions; tetrabutylammonium hydroxide (ITBA) in amounts equal to 500 ppm, had been dissolved.

The resulting mixture was heated in an oil bath to 95 °C; the pH was adjusted at a value of about 3.0 by means of small additions of a 15% H_2SO_4 aqueous solution or of a 10% NaOH aqueous solution. The mixture was intensely stirred in order to dissolve all PCF, TCF, or PECF. Then, a H_2O_2 aqueous solution (50% by volume) was gradually added at a rate of about 0.2 ml/min. After programmed additions of H_2O_2 - (as indicated in Table VII), reaction mixture samples (5 ml each) were drawn for analysis. For each sample, the residual PCF, TCF, or PECF concentration ([PCF], [TCF], [PECF]), the COD and the chlorine ion concentration ($[Cl^-]$) were determined according to the above described modalities. The results are reported in Table VII, where also the mineralization per cent (%$[Cl^-]$) is indicated, expressed as ratio between the actually obtained Cl^- ion concentration and the maximum obtainable Cl^- ion concentration.

During the reaction, the pH was maintained around 3.0 by means of small additions (0.1-0.2 ml) of the NaOH or H_2SO_4 solutions, while the temperature was maintained constant at 97 °C.

TABLE I

H_2O_2 (g/l)	EX. 1 ([ITBA] = 150 ppm)			EX. 2 ([ITBA] = 300 ppm)			EX. 3 ([ITBA] = 0 ppm)		
	[PCBs] (ppm)	$[Cl^-]$ (ppm)	%$[Cl^-]$	[PCBs] (ppm)	$[Cl^-]$ (ppm)	%$[Cl^-]$	[PCBs] (ppm)	$[Cl^-]$ (ppm)	%$[Cl^-]$
0	3431	0 (1621)*	0	4532	0 (2142)*	0	3431	0 (1621)*	0
2.62	1463	110	6.8	-	-	-	3400	0	0
6.57	877	148	9.1	-	-	-	3400	0	0
13.13	490	250	15.4	-	-	-	3400	0	0
18.4	-	-	-	1922	-	-	3400	0	0
36.6	-	-	-	1245	-	-	3400	0	0
73.3	-	-	-	804	-	-	3400	0	0
91.7	-	-	-	288	<5	-	3400	0	0
183	-	-	-	30	51	2.4	3400	0	0

* maximum obtainable concentration of Cl^- ions.

TABLE II

H_2O_2 (g/l)	EX. 4 ([TBAB] = 150 ppm)			EX. 5 ([TBAB] = 472 ppm)			EX. 6 ([TBAB] = 0 ppm)		
	[PCBs] (ppm)	$[Cl^-]$ (ppm)	% $[Cl^-]$	[PCBs] (ppm)	$[Cl^-]$ (ppm)	% $[Cl^-]$	[PCBs] (ppm)	$[Cl^-]$ (ppm)	% $[Cl^-]$
0	3000	0 (1489)*	0	3000	0 (1489)*	0	3000	0 (1489)*	0
6.27	157	-	-	2247	-	-	3000	-	-
31.37	33	-	-	1841	-	-	3000	-	-
62.7	12	-	-	1800	-	-	3000	-	-
125.5	4.5	104	7	1019	22	1.4	3000	0	0

* maximum obtainable concentration of Cl^- ions.

TABLE III

H_2O_2 (g/l)	EX. 7 ([TBAI] = 166 ppm)			EX. 8 ([TBAI] = 460 ppm)			EX. 9 ([TBAI] = 0 ppm)		
	[PCBs] (ppm)	$[Cl^-]$ (ppm)	%$[Cl^-]$	[PCBs] (ppm)	% $[Cl^-]$ (ppm)	%$[Cl^-]$	[PCBs] (ppm)	$[Cl^-]$ (ppm)	%$[Cl^-]$
0	2700	0 (1276)*	0	2700	0 (1276)*	0	2700	0 (1276)*	0
6.27	1832	-	-	2435	-	-	2700	-	-
31.37	1155	-	-	2135	-	-	2700	-	-
62.7	630	-	-	1520	-	-	2700	-	-
125.5	145	48	3.6	-	20	1.5	2700	0	0

* maximum obtainable concentration of Cl^- ions.

TABLE IV

H_2O_2	EX. 10 ([ITBA] = [TBAB] = 100 ppm)			EX. 11 ([ITBA] = [TBAB] = 0 ppm)		
	[PCBs] (ppm)	$[Cl^-]$ (ppm)	%$[Cl^-]$	$[Cl^-]$ (ppm)	$[Cl^-]$ (ppm)	%$[Cl^-]$
0	2950	0 (1276)*	0	2950	0 (1276)*	0
125.5	10	292	23	2950	0	0

* maximum obtainable concentration of Cl^- ions

TABLE V

EX.12		[PCBs] (mg)	[PCBs] (ppm)	[Cl^-] (ppm)	% [Cl^-]
PAPER (CH_2Cl_2 extract)	initial	21.22	1060	(465)*	-
	final	2.05	102	-	-
AQUEOUS PHASE (reaction end)	as such	0	0	127	27.3
	CH_2Cl_2 extract	0	0	-	-

* maximum obtainable concentration of Cl^- ions

TABLE VI

H_2O_2 (stoich. equiv.)	EX.13				EX.14		
	[ECE] (ppm)	COD (mg/l)	$[Cl^-]$ (ppm)	% $[Cl^-]$	[MDB] (ppm)	$[Cl^-]$ (ppm)	% $[Cl^-]$
0	5000	4124	0 (3690)*	0	5000	0 (2413)*	0
2	12	900	1955	53,5	0	1710	71
4	10	700	2933	80,2	-	-	-
5	-	-	-	-	0	1905	80
7,7	0	550	3687	99,9	-	-	-
10	-	-	-	-	0	2052	85

* maximum obtainable concentration of Cl^- ions

TABLE VII

H_2O_2 (stoich. equiv.)	EX.15				EX.16				EX.17			
	[PCF] (ppm)	COD (mg/l)	$[Cl^-]$ (ppm)	% $[Cl^-]$	[TCF] (ppm)	COD (mg/l)	$[Cl^-]$ (ppm)	% $[Cl^-]$	[PECF] (ppm)	$[Cl^-]$ (ppm)	% $[Cl^-]$
0	25000	39150	0 (6850)*	0	1000	1475	0 (550)*	0	1000	0 (666)*	0
0,2	1000	22250	-	-	686	1250	241	44	350	0	-
0,5	0	19500	-	-	-	-	-	-	262	0	-
1	0	3000	6846	99	200	900	377	69	125	0	-
1,5	-	-	-	-	100	150	538	99	-	-	-
13	-	-	-	-	-	-	-	-	0	385	58
83	-	-	-	-	-	-	-	-	0	612	92

* maximum obtainable concentration of Cl^- ions

Claims

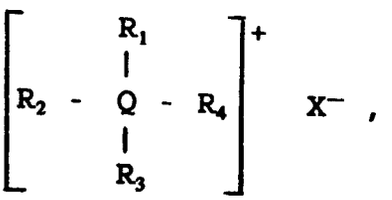
1. A process for the disposal of chlorinated organic products, which comprises treating said products with a H_2O_2 aqueous solution, in the presence of Fe(II) ions, optionally in association with one or more

transition metal ions selected from Cu(II), Ti(IV), Mn(II), Co(II), Ni(II), W(IV) and Mo(IV), and in the presence of a phase transfer agent.

2. The process of claim 1, wherein the chlorinated organic products have aromatic, alkyl-aromatic, olefinic, aliphatic or cycloaliphatic structure.

3. The process of claim 2, wherein the chlorinated organic products are selected from: polychlorobiphenyls (PCBs), chlorobenzenes, chlorophenols, 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT), trichloroethylene, perchlorobutadiene, tetrachloroethane, hexachlorocyclohexane, hydrated chloral, hexachloroethane, perchloroacetone.

4. The process of any of the preceding claims, wherein the phase transfer agent is selected from ammonium, phosphonium or arsonium salts of general formula:



wherein:
Q is selected from N, P and As;
R_1, R_2, R_3 and R_4, like or different from one another, are selected from: hydrogen, C_1-C_{35} alkyl groups, C_6-C_{10} aryl groups, C_1-C_{10} arylalkyl or alkylaryl groups, provided that at least one of R_1, R_2, R_3 and R_4 is different from hydrogen;
X^- is selected from OH^-, Cl^-, Br^-, I^- and BH_4^-.

5. The process of claim 4, wherein the phase transfer agent is selected from tetraalkylammonium salts, in which the alkyls, like or different from each other, have 1 to 35 carbon atoms.

6. The process of any of the preceding claims, wherein the phase transfer agent is utilized in a concentration, referred to the aqueous phase, ranging from 20 to 500 ppm.

7. The process of claim 6, wherein the chain transfer agent is utilized in a concentration, referred to the aqueous phase, ranging from 100 to 300 ppm.

8. The process of any of the preceding claims, wherein the Fe(II) ions are utilized in a concentration, referred to the aqueous phase, ranging from 50 to 1,000 ppm.

9. The process of any of the preceding claims, wherein the Cu(II), Ti(IV), Mn(II), Co(II), Ni(II), W(IV) or Mo(IV) ions are utilized in a concentration, referred to the aqueous phase, ranging from 0 to 400 ppm.

10. The process of any of the preceding claims, wherein Fe(II) ions and one or more transition metal ions selected from Cu(II), Ti(IV), Mn(II), Co(II), Ni(II), W(IV) and Mo(IV) are utilized in equimolar amounts, each in a concentration ranging from 50 to 400 ppm.

11. The process of any of the preceding claims, wherein the H_2O_2 aqueous solution is utilized in such amounts that the molar ratio of added H_2O_2 to initially present chlorinated organic product ranges from 0.2 to 100.

12. The process of claim 11, wherein the molar ratio of added H_2O_2 to initially present chlorinated organic product ranges from 0.2 to 30.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 4665

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y	US-A-4 693 833 (M.TOSHIKUNI ET AL.) * the whole document * ---	1-12	A62D3/00
Y	US-H-366 (R.P.SEIDERS) * column 1, line 1-11 * * column 1, line 60 - column 2, line 1 * * column 2, line 63-68 * ---	1-12	
A	US-A-5 004 551 (K.L.SUBLETTE) * the whole document * ---	1-12	
A	DATABASE WPI Week 7841, Derwent Publications Ltd., London, GB; AN 78-73285A & JP-A-53 099 657 (MITSUBISHI HEAVY IND.) * abstract * ---	1-12	
A	EP-A-0 109 273 (MONTEDISON) -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			A62D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 January 1994	DALKAFOUKI, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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