

**Process for preventing contamination of the aquatic
environment with organisms from another locality**

Description

The invention relates to a process for preventing contamination of navigable waters with organisms from the series of zooplankton including the epifauna thereof and of phytoplankton including the resting stages thereof (cysts) which are taken up with the ballast water of ships and transferred to another place when the ballast water is discharged. The process comprises the addition of an agent containing a peroxygen compound to the ballast water, allowing the agent to react in a concentration and for a period such that the organisms are substantially destroyed, and introduction of the ballast water thus treated into the aquatic environment.

Shipping has experienced considerable structural changes in recent years. In container shipping in particular, ship sizes, lay days, loading strategies and hence the quantities of ballast water, the residence times thereof and the mixing ratios thereof in harbour and coastal areas have been altered considerably so that new scenarios have arisen which imply new risks for the transfer of exotic species and bacteria which are pathogenic for humans. In recent years in particular, it has been confirmed on the basis of drastic examples that such organisms are being transferred with the ballast water from ships to other places with far-reaching consequences for ecology and health. One example is the appearance of the zebra mussel in the Great Lakes of North America. This has both led to a change in the food structure with consequences for fishing and tourism and burdened the energy industry with high costs of combating the mussel in power station cooling circuits. Lasting and in some cases irreparable long-term damage is also being caused by the massive transfer of

9905994-1

29 NOV 1999

resting cysts of toxic algae which not only leads to unwanted bloom but also endangers the cultivation of mussels and oysters in many coastal regions. Finally, the transfer of a species akin to the jellyfish to the Black Sea a few years ago led to the complete collapse of sardine fishing. The intercontinental transfer of infectious bacteria which are pathological for humans, such as *Vibrio Cholearae*, serotype 01 L, has been proved by the Institute for Molecular Biology, Baltimore, USA. These examples show that there is an urgent need for action to develop measures for reducing the risk of transferring exotic plant and animal organisms and pathological bacteria with the ballast water of ships.

There has been no lack of attempts to develop suitable methods for treating ballast water of ships. These were unable to become established because of insufficient effectiveness and/or shortcomings. Although microorganisms can be destroyed by treating the water with strong UV radiation, said radiation does not kill larger organisms contained in zooplankton such as *Artemia*, crabs, mussels and the eggs thereof. Moreover, UV technology also necessitates expensive pumping of the ballast water.

Ozone is an effective biocide but ozonation of the ballast water of ships is technically too complex. Treatment of the ballast water with hypochlorite has the disadvantage of the formation of organochlorine compounds, the poor stability of hypochlorite, and the corrosiveness thereof.

Many organic compounds are known which are highly effective biocides but their long-term effect or their high stability is not desirable for use in ballast water: After treatment it should be possible to feed the biocides with the ballast water in a largely degraded and ecologically harmless form into the aquatic environment. The transit times of a ship and hence the treatment time of the ballast water may range

from a few days to many weeks, so control of the residual biocide content is no longer guaranteed.

It is well known that hydrogen peroxide, which decomposes to water and oxygen, has a biocidal effect on certain microorganisms but mostly only a biostatic effect. The oxidation potential of hydrogen peroxide is generally too low to damage organisms of the zooplankton effectively or to kill them. A process for preventing contamination of navigable waters by cysts of harmful plankton is described in US patent 5,256,423, which process consists in adding an effective amount of hydrogen peroxide to the ballast water and discharging the ballast water only after a sufficiently long reaction time during which the cysts are substantially destroyed. The cysts which can be destroyed by this process are resting stages of the algae belonging to the phytoplankton. As practical experience has shown, the spectrum of action of hydrogen peroxide is not sufficient for treating ballast water because other organisms of the phyto- and zooplankton, including their resting stages which are also situated in the ballast water, are not destroyed sufficiently, if at all.

It is known from US patent 5,393,781 that the zebra mussel in the adult and larval form can be controlled by contact with peracetic acid. A solution containing peracetic acid in an effective amount is added, for example, to a water inlet or a storage vessel of a water treatment plant. The use of a peracetic acid solution for the treatment of ballast water of ships in order to prevent the transfer of species of organism from another locality from one aquatic environment to another is neither disclosed nor suggested in said document. Nor does it disclose whether and on what scale the eggs of zebra mussels and of other organisms of the zooplankton including the epifauna thereof are destroyed by peracetic acid.

The object of the present invention is, therefore, to show a process for effectively preventing the transfer of harmful organisms from the series of zooplankton including the epifauna thereof and of phytoplankton including the resting stages thereof with the ballast water of ships. The process should make it possible, apart from the well known combating of cysts and zebra mussels, effectively to destroy other organisms taken up with the ballast water. According to a further object, it should be possible to carry out the process using an agent which can be decomposed sufficiently quickly for no ecotoxicological problems to occur when the ballast water is discharged.

A process was found for preventing contamination of navigable waters with organisms from the series of zooplankton including the epifauna thereof and of phytoplankton including the resting stages thereof (cysts) which are taken up with the ballast water of ships and transferred to another place when the ballast water is discharged, comprising the addition of an agent containing a peroxygen compound to the ballast water, allowing the agent to react until the organisms are substantially destroyed, and introduction of the ballast water thus treated into the aquatic environment, which is characterised in that the agent contains, as a peroxygen compound, a water-soluble percarboxylic acid with 1 - 6 C atoms and in that the agent is added in a quantity corresponding to 0.1 to 200 mg of percarboxylic acid per litre of ballast water.

The subclaims relate to preferred embodiments.

The term plankton means all the animal and plant organisms in all their forms suspended in water. The term zooplankton thus means organisms in egg form, larval form and adult form. The term "phytoplankton" also means the resting stages of the organisms such as cysts. The organisms to be

destroyed in the ballast water are primarily representatives of the following taxonomic groups: unicellular algae, the physiology of which resembles that of toxic red tide algae. The zooplankton organisms to be destroyed are primarily copepods and their larval stages, representatives of the vagiel benthos fauna including Crustacea of various stages of life, and also larval and egg stages of mussels, crustaceans and fish; organisms of the series of coelenterates, rotifers, tunicates, pteropods and larval stages of sponges, nemertines, molluscs, annelids, bryozoa and echinoderms may also be contained in the ballast water - destruction of said organisms in the ballast water is also desirable for the prevention of transfer.

It has been found that by treating ballast water with a percarboxylic acid, also known as peroxydicarboxylic acid, very different organisms of the generic kind may be destroyed. The percarboxylic acid acts as a biocide and has a broad spectrum of action. The term "substantially destroyed" means a rate of destruction of generally at least 90%, preferably more than 99% and a reduction in the hatching rate of eggs by at least 50%. Although a 100% destruction rate may be obtained without difficulty in vitro, a 100% destruction rate is not always guaranteed in practice, nor is it absolutely necessary, in view of the size of the ballast chambers in the ship, the dead spaces which cannot be excluded, and a possibly incomplete mixing of the small amount of biocidal agent with the large amount of ballast water.

The biocidal agent to be added to the ballast water may contain one or more percarboxylic acids. Said agent is usually an aqueous solution which may also contain, apart from the one or more percarboxylic acids, other active biocides and/or other auxiliaries such as, e.g., surfactants.

The agents to be used according to the invention contain a water-soluble percarboxylic acid with 1 to 6, preferably 1 to 3 carbon atoms. The percarboxylic acid may have one or two peroxy-carboxyl groups and, if necessary, also one or two hydroxyl groups. Examples of suitable percarboxylic acids are performic acid, peracetic acid, perpropionic acid, perlactic acid, pertartaric acid, mono- and diperoxy-succinic acid, mono- and diperoxyglutaric acid and mono- and diperoxyadipic acid. In particular preference the biocidal agents to be used contain peracetic acid, performic acid, perpropionic acid or mixtures of said percarboxylic acid, particularly mixtures of peracetic acid and performic acid. An effective peracid combination contains at least two of the above-mentioned peracids of dicarboxylic acids.

Normally, the biocidal agent containing one or more percarboxylic acid also contains hydrogen peroxide and the carboxylic acids on which the percarboxylic acids present are based. Such mixtures result from the preparation of the agents containing percarboxylic acid by reaction of one or more carboxylic acids with an aqueous hydrogen peroxide solution. An agent which can be obtained in this way may be used before or after the equilibrium is reached. An agent based on a so-called equilibrium percarboxylic acid solution is used in particular preference, particularly an equilibrium peracetic acid solution to which one or more other biocidal components and/or auxiliaries were added prior to use.

According to a preferred embodiment, the biocidal agent used is a solution containing peracetic acid, performic acid, acetic acid, formic acid, hydrogen peroxide and water in a total quantity of at least 95 wt.%. Due to the preparation, such a solution may also contain a mineral acid catalyst and active oxygen stabilisers. Such a

solution may be obtained in a simple manner by adding formic acid to a solution containing peracetic acid, acetic acid, hydrogen peroxide and water, for example, a 1 to 35 wt.%, particularly 1 to 15 wt.% equilibrium peracetic acid, or by adding a water-soluble formate to an equilibrium peracetic acid solution containing mineral acid as catalyst. Performic acid is more effective compared with peracetic acid, but also more susceptible to decomposition. Advantageously, therefore, formic acid is added to the solution containing peracetic acid only prior to use and the mixture is added to the ballast water after a reaction time lasting some hours. It is also possible to add a solution containing peracetic acid as the sole percarboxylic acid and formic acid separately to the ballast water; the efficiency of this combination is higher than that of the solution containing exclusively peracetic acid, but lower than that obtained using a solution containing peracetic acid and performic acid.

Other biocidal substances instead of formic acid may also be added to the agent containing carboxylic acid or immediately to the ballast water. Suitable biocides of this kind are acrolein-cleaving acetals, for example, 2-vinyl-1,3-dioxolane or 2-vinyl-1,3-dioxane. Whereas the acid content of a percarboxylic acid solution is sufficient to cleave the acetal, it is advantageous, if the acetal is added directly to the ballast water, to use the acetal in combination with an acid or an acid-cleaving agent.

According to a further embodiment, an alkali metal cyanide is added in a small quantity to the ballast water apart from an agent containing percarboxylic acid. The cyanide is used advantageously in a quantity of about 0.1 to 20 mg per litre of ballast water. The use quantity of the agent containing percarboxylic acid, to which the cyanide may also be added directly, if necessary, is from 0.1 to 200 mg, particularly 1 to 100 mg and particularly preferably 1

to 30 mg of percarboxylic acid per litre of ballast water. According to a particularly preferred embodiment of the combined use of a percarboxylic acid solution and a cyanide, 5 to 100 mg of a 1 to 15 wt.% equilibrium peracetic acid and, together with said acid or separately, at the same time or after a certain delay, 1 to 5 mg cyanide per litre of ballast water are added to the ballast water.

It has been found that the combined use of an agent containing percarboxylic acid and a cyanide leads to a synergistic effect. Whereas the eggs of many organisms belonging to the zooplankton are not destroyed satisfactorily either by the sole use of a solution containing percarboxylic acid or by the use of a cyanide, the combined use of the two substances proves very effective. Due to the above-mentioned combination it is also possible to reduce the concentration of percarboxylic acid. Whereas the sole use of a cyanide brings about an effective destruction of adult animals, the eggs of certain organisms survive; on the other hand, adult animals of certain organisms are incompletely destroyed by the sole use of a percarboxylic acid, though the eggs thereof are destroyed.

In the event of the combined use of an equilibrium peracetic acid and formic acid where, as mentioned above, the formic acid may be added directly to the peracetic acid or at the same time as this to the ballast water, the use quantity of formic acid corresponds to 10 to 1000 wt.%, based on the sum of peracetic acid and acetic acid.

The agent containing percarboxylic acid or a combination thereof with further biocides may be added to the ballast water by a single addition or multiple additions. If necessary, a certain content of percarboxylic acid is maintained in the ballast water until substantially all the

organisms in the adult, larval or egg form are destroyed. After the addition of the biocidal agent, the ballast water is kept in the ballast tanks of the ship until the destruction is substantially complete; only afterwards is the ballast water discharged and fed to the aquatic environment. According to an alternative procedure, the ballast water may also be fed directly to a tank farm provided for this purpose in the harbour area and treated according to the invention in said tank farm.

The process according to the invention makes it possible effectively to prevent the transfer of unwanted organisms from one place to another. The agents to be used are used in a concentration such that either they are degraded after fulfilling their task or they may be discharged as an ecotoxicological substance. The biocidal substances to be used according to the invention are used advantageously in a quantity such that, after the scheduled transit time, the population of organisms in the ballast water is destroyed. Accordingly, if the transit time is short, the concentration of effective biocides will be higher than if the transit time is long. Even in the event of the combined use of a solution containing percarboxylic acid and a cyanide, an excessive cyanide concentration in the ballast water to be discharged is avoided by the fact that the cyanide is oxidised to harmless substances by the percarboxylic acid present.

The examples below show the effectiveness in principle of the solutions containing percarboxylic acid on the survival rate of selected test organisms under defined conditions.

Examples B1 to B6 and comparison examples VB1 to VB4

Tests were carried out on *Artemia salina* (crustaceans) as test organism, namely in the egg, larval and adult stage of life. The medium examined was North Sea water with a

salinity of 3.3% and the fixed temperature was room temperature (about 20°C). The adult *Artemia* were kept in 5 litre sea water tanks; the *Artemia* eggs and larvae were kept in 2 ml screw top jars. The mortality was determined from the survival rates of the adult animals and nauplii over an exposure time of up to 72 hours. The tests were carried out in three parallel groups. In the case of the eggs, the hatching rate (%) was determined after the stated times.

The following active substances and combinations were tested:

- A: Equilibrium peracetic acid containing 5 wt.% peracetic acid, 27.5 wt.% hydrogen peroxide and 5.5 wt.% acetic acid, prepared from acetic acid and aqueous hydrogen peroxide in the presence of 2 wt.% sulfuric acid.
- B: Mixture of a solution according to A with 85 wt.% formic acid in a mixing ratio of 1 to 1. The mixture was used after being left to stand for 1 hour.
- C: Mixture of a solution according to A with a combination of 2-vinyl-1,3-dioxolane with maleic anhydride (1:1) (= VDL-K). Mixing ratio of A to VDL-K equals 100:1. The mixture was used immediately after preparation.

Table 1 shows the mortality in % of adult *Artemia salina* - means of three parallel tests in each case using agents A, B, C and VDL-K in the given concentrations c (mg/l). The control contained 60 animals, the samples treated with an agent according to the invention contained 150 animals.

Table 1:

Example	VB 1	B 1	B 2	B 3	VB 2
Time (h)	Control	A	B	C	VDL-K
		2000 mg/l	2000 mg/l	2000 mg/l	20 mg/l
0.5	0	0	0.7	0	0
1	0	0	12.7	0	0
2	0	0	73.3	8	0.7
3	0	3	96.7	18	2
5	2	9	100	32	8
7	2	13	100	100	42
10	3	24	100	100	51
24	3	84	100	100	100
48	3	92	100	100	100
72	3	97	100	100	100

Table 2 shows the mortality in % of larval *Artemia salina* (nauplii) after exposure. The means of 3 parallel tests and the total figures for the test organisms per test group are given.

The mortality of the adult *Artemia* reached only 97% using the test concentration of A, whereas the effect of B and C is much more rapid and quantitative.

Table 2:

Example	VB 3	B 4	B 5	B 6	VB 4
Time (h)	Control	A 2000 mg/l	B 2000 mg/l	C 2000 mg/l	VDL-K 20 mg/l
	n = 182	n = 211	n = 122	n = 195	n = 211
0.5	0	0	0.5	0	0
1	0	0	91.6	0	0
2	0	1	100	2	1
3	0	1	100	50	21
5	0	23	100	100	97
10	0.5	73	100	100	100
24	0.5	100	100	100	100
48	0.5	100	100	100	100
72	0.5	100	100	100	100

Example 7

When resting eggs of *Artemia salina* were exposed to the active substances A, B and C and the above-mentioned active substance concentrations, no larva development takes place.

Example 8

The test organisms used were adult shrimps (*Mysis* sp) which were exposed to the active substance according to A (c = 2000 mg/l). After only 0.5 h, the mortality was 100%.

Examples 9 and 10

The active substances used were: Sodium cyanide and the equilibrium peracetic acid solution used above (E-PAA) (= A). In examples 9 and 10, the cyanide (CN) and the E-PAA were added separately but simultaneously to the water with the adult *Artemia*, nauplii and resting eggs of *Artemia*. The use quantities per litre of water were 3.3 mg of NaCN and 10 mg of E-PAA in example 9 (formulation A) and 46.3 mg of

NaCN and 50 mg of E-PAA in example 10 (formulation A).

Table 3 shows the results - mortality and hatching rate in %.

Table 3:

Example	9a	9b	10*)
Test	Adult nauplii		Eggs
Artemia			
Time (h)	Mortality (%)		Hatching rate (%)
1	0	0	0
2	0	2.1	
5	13.3	12.8	
16	66.7	97.9	20
24	96.7	100.0	30

*) Control hatching rate without active substances:

1 h, 40 %; 14 h 90 %; 24 h 95 %



Patent claims

1. Process for preventing contamination of navigable waters with organisms from the series of zooplankton including the epifauna thereof and phytoplankton including the resting stages thereof (cysts) which are taken up with the ballast water of ships and transferred to another place when the ballast water is discharged, comprising the addition of an agent containing a peroxygen compound to the ballast water, allowing the agent to react until the organisms are substantially destroyed, and introduction of the ballast water thus treated into the aquatic environment, characterised in that the agent contains, as peroxygen compound, a water-soluble percarboxylic acid with 1 to 6 C atoms and in that the agent is added in a quantity corresponding to 0.1 to 200 mg of percarboxylic acid per litre of ballast water.
2. Process according to claim 1, characterised in that the agent used contains at least one percarboxylic acid from the series comprising performic acid, peracetic acid and perpropionic acid and also an agent containing hydrogen peroxide.
3. Process according to claim 1 or 2, characterised in that the agent used is based on a so-called equilibrium peracetic acid with a peracetic acid content of 1 to 10 wt.%.
4. Process according to one of claims 1 to 3, characterised in that an agent containing peracetic acid, performic acid,



acetic acid, formic acid, hydrogen peroxide and water in a total quantity of at least 95 wt.% is used.

5. Process according to one of claims 1 to 4, characterised in that in addition to the agent containing a percarboxylic acid, one or more other biocidal compounds are added to the ballast water or in that the other biocidal compounds are already added to the agent containing percarboxylic acid before the addition thereof to the ballast water.
6. Process according to claim 5, characterised in that the other biocidal compound used is formic acid, a cyanide or an acrolein-liberating acetal.
7. Process according to claim 5 or 6, characterised in that cyanide is used in a quantity of 0.1 to 20 mg per litre of ballast water.
8. Process according to one of claims 1 to 7, characterised in that, per litre of ballast water, 5 to 100 mg of a 1 to 15 wt.% equilibrium peracetic acid and, together with said equilibrium peracetic acid or separately, at the same time or after a certain delay, 1 to 5 mg of cyanide are added to the ballast water.
9. Process according to one of claims 1 to 8, characterised in that the agent containing percarboxylic acid and optionally the other biocidal compound(s) also added to the ballast water are allowed to react for such a time before the ballast water is introduced into the aquatic environment and, if necessary, the agent and



the other biocidal compounds are metered in afterwards, until at least 99% of the organisms are destroyed.

10. Process according to one of claims 1 to 9, characterised in that the treatment of the ballast water for the purpose of destroying the organisms is carried out on board the ship, particularly during the journey thereof or, after the ballast water has been discharged, in a treatment plant on land, and the treated ballast water is introduced into the aquatic environment in the filtered or unfiltered state.