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(54) ANTIMICROBIAL AGENTS

(71) We, HENKEL KOMMANDITGESELLSCHAFT AUF AKTION, a German Company, of 67 Henkelstrasse, 4000 Duesseldorf - Holthausen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

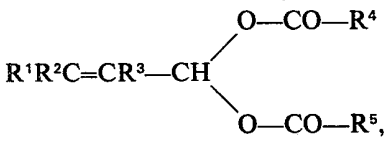
The present invention relates to antimicrobial agents.

Industrial water and other domestic waters, such as the water in swimming baths, coolant circuit water, washer water in air conditioning plants and the like, tend to be infested by micro-organisms. When the mass development of these micro-organisms is undisturbed, incrustations are formed, thus causing a reduction in the heat exchanger in cooling plant, blockages or at least considerable reductions in the rates of flowthrough, corrosion and the formation of unpleasant odours. The germs which are generally the most troublesome in industrial and other domestic waters are algae, slime-forming bacteria and sulphate-reducing bacteria.

Thus, endeavours have been made for a long time to discover methods and products for preventing the development of such micro-organisms in the various domestic waters. These endeavours have led to the use of a large number of substances, but without finding a solution to the problem which is satisfactory in every respect. Quaternary ammonium compounds are among the products which, in practice, are perhaps those mose frequently used as biocides in industrial waters and swimming baths. When used in low concentrations, these quaternary ammonium compounds exhibit an unsatisfactory action against typical Gram-negative water germs and sulphate-reducing bacteria. However, their considerable tendency to form foam stands in the way of their use in concentrations which might lead to satisfactory antimicrobial efficacy.

Thus, the task arose of providing agents of great efficacy, which do not have the said disadvantages, for the preservation of industrial and other domestic waters.

The novel antimicrobial agents for the preservation of industrial and domestic waters are characterised by a content of diacylates of aliphatic unsaturated aldehydes of the general formula



in which R^1, R^2 and R^3 represent hydrogen radicals and alkyl radicals having less than 8 carbon atoms and may be the same or different, and R^4 and R^5 may also be the same or different and represent aliphatic radicals having up to 6 carbon atoms or represent phenyl radicals, and a water-soluble polymer of acrylic acid and/or derivatives thereof having a molecular weight of 500 to 50,000 or a water-soluble block polymer of ethylene oxide/propylene oxide as dispersing agent.

Among the diacylates of aliphatic unsaturated aldehydes which thus come under consideration, 3,3 - diacetoxy - 1 - propene has proved to be particularly suitable.

This compound is antimicrobially effective against virtually all germs, such as Aerobacter aerogenes, E. Coli, PS. aeruginosa, PS. fluorescens, which occur in technical water systems, and against slime-formers and spore-formers.

However, it is essential to the efficacy of the antimicrobial agents when used in practice that they also contain a dispersing agent based on a water-soluble low-molecular polymer of acrylic acid and/or derivatives thereof, or based on a water-soluble block polymer of ethylene oxide/propylene oxide.

In particular, polymers of acrylic acid,

methacrylic acid or acrylamide having molecular weights of between 500 to 50,000 are suitable. The molecular weight of the water-soluble block polymers of ethylene oxide/propylene oxide can fluctuate between 500 and 10,000. If desired, small quantities of interlacing agents such as fatty acid polyglycolether or fatty alcohol sulphates may be added.

The antimicrobial agents in accordance with the invention are added in small quantities to the water to be treated. The quantity of the microbicide component is 10 to 1,000 mg/l, preferably 50 to 500 mg/l, and the quantity of the dispersing component is from 50 to 500 mg/l. The biocide component and the dispersing component are used in the weight ratio of 10:1 to 1:1.

The following Table shows the antimicrobial efficacy of the composition.

Germ	Dosage[+] (ppm)	Reaction period (hours)	Destruction (%)
Aerobacter	120	4	99.7
aerogenes	60	24	99.8
E. Coli	120	24	90
PS. aeruginosa	600	1	99.8
	600	4	99.9
	60	24	99.8
PS. fluorescens	600	1	99.0
	600	24	100.0
	60	24	99.9
White slimeformers	120	24	100.0
	60	24	97.7

[+]Ratio of biocide component (3,3 - diacetoxy - 1 - propene): dispersing component (ethylene oxide/propylene oxide/block polymer, molecular weight 2,000) is 5:1.

The advantages of the combination of diacylates with the said dispersion agents resides, inter alia, in the increased synergistic attack of the diacylate on the biological material. This leads to a very rapid reduction in the growth. Conversely, the dispersing effect of the dispersing agent is promoted by the diacylate component. Owing to the very low dosages of both the dispersing agent and the diacylate, there is a minimal loading of the drainage canal.

Furthermore, the diacylate has the advantage that it can be satisfactorily decomposed biologically with appropriate dilution.

The present invention will now be further described by means of the following Examples.

Example 1

A sample of circulating water from a refinery having a high content of hydrocarbons was incubated at 30°C in a thermostatically-controlled shaker by adding water germs. Each sample was at the same time aerated in order to obtain rapid growth of the germs. The germ account in all the samples was 10^8 germs/ml after 20 days and comprised the following: yellow and white slime-formers brownish Pseudomonadaceae, Pseudomonas aeruginosa and aerobic spore formers, as well as non-definable germs.

3,3 - diacetoxy - 1 - propene in a concentration of 250 ppm, and 50 ppm of polymeric acrylic acid the molecules of which have molecular weights ranging from 1000 to 10,000 with a preponderance of molecules having a molecular weight of substantially 4000, were added to this water. The terms were reduced by one power of 10 after 3 hours and by four powers of 10 after 5 hours. The total germ count had dropped to 10 germs/ml after 24 hours.

The same test with a dosage of 100 ppm of the biocidal compound resulted in a residual germ count of 10^2 germs/ml after 24 hours.

This low number of germs is excellent for industrial service water systems.

Example 2

A technical cooling system having a capacity of 800 m^3 had a high germ count of 4×10^8 germs/ml, considerable growths of slime-formers having occurred particularly on the walls of the pipes and the surfaces of the heat exchanger. This circulating system was treated with the following dose of a composition, in accordance with the invention, comprising the antimicrobial effective substance and further dispersing agents:

Biocide (as in Example 1) 100 ppm
Dispersing agent[+] 50 ppm

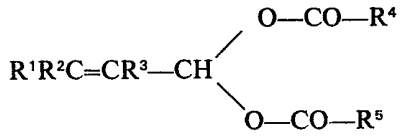
[+]An ethylene oxide/propylene oxide block polymer having a mean molecular weight of 2,000.

Interlacing agent
(fatty alcohol ethoxylate) 10 ppm

The turbid substances in the circulating water were measured 3 hours after commencement of the dosing. There was a considerable increase in the content of turbid substances by approximately 1 power of 10. These turbid substances are composed of dispersed slime-formers. The germ count in the circulating water dropped to values of approximately 2×10^2 germs/ml in the course of 24 hours. The walls of the pipes were virtually free from large incrustations and growths.

WHAT WE CLAIM IS:—

1. An antimicrobial composition for the preserving of industrial and domestic water, comprising diacylate of an aliphatic unsaturated aldehyde of the general formula



in which R^1, R^2 and R^3 represent hydrogen or alkyl radicals having less than 8 carbon atoms and may be the same or different, and R^4 and R^5 may also be the same or different and represent aliphatic radicals having up to 6 carbon atoms or phenyl radicals, and a water-soluble polymer of acrylic acid and/or derivatives thereof, having a molecular weight of 500 to 50,000 or a water-soluble block polymer of ethylene oxide/propylene oxide as dispersing agent.

2. A composition as claimed in claim 1 in which the diacylate of the general formula is 3,3 - diacetoxy - 1 - propene.

3. A composition as claimed in claim 1 and substantially as hereinbefore described with reference to Example 1 or 2.

4. A method of preserving industrial and domestic water comprising adding to the water a quantity of 10 to 1,000 mg/l of a diacylate of an aliphatic unsaturated aldehyde as defined in claim 1 and 50 to 500 mg/l of a dispersing agent as defined in claim 1, the weight ratio of the diacylate to the dispersing agent being 10:1 to 1:1.

5. A method as claimed in claim 4 and substantially as hereinbefore described with reference to Example 1 or 2.

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