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(54) SLIME-CONTROLLING AGENT

- (71) We, KURITA WATER INDUSTRIES LTD., a Japanese body corporate of No. 1, 3-chome, Koraihashi, Higashi-ku, Osaka-shi, Japan, 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 slime-controlling agents for use in preventing adhesion of slime, caused by, *inter alia*, microbial organic matter in industrial water, more particularly in the cooling water of heat exchangers employed in various plants.
- The shortage of industrial water supply recently has led to the introduction of circulating systems for the cooling water of heat exchangers and the like, not only in the field of chemical industry but also at various other plants, while, on the other hand, the quality of the water which is used for such cooling water and other purposes is deteriorating as the contamination of river water worsens.
- It is well-known that employment of contaminated cooling water in a circulating system gives rise to the formation of an adhering material, consisting mainly of microbial matter, so-called slime, on the inner surfaces of the heat exchanger or the like. In extreme cases, clogging of the heat exchanger itself occurs, so that the thermal conductivity of the heat exchanger may be lowered by an amount sufficient to cause serious interference with the operation of plants in the line of the cooling-water circulating system, thus causing a loss in production efficiency. Moreover, adhesion of this slime onto the surface of a heat exchanger results in the formation of a local electric cell, due to the difference in oxygen concentration; even in the presence of a satisfactory quantity of a corrosion inhibitor, this may give rise to a pitting or corrosion of the cell.
- Such being the case, it is very desirable to prevent even a slight adhesion of slime, from the viewpoint of maintenance of the thermal conductivity of the heat exchanger, as well as

prevention of corrosion thereof. However, the occurrence of obstruction of pipes and equipment attributable to this slime has so far been frequent, not only in cooling-water circulating systems but also in many other plants in which there is contact with water.

Because the occurrence of problems caused by slime is attributable to the aggregations (or floculations) of microbes formed in water which adhere to the surface of metal, the employment of microbicides has been popular in controlling slimes. That is to say the formation of microbial aggregations had been attacked by using the germicidal properties of such microbicides so as to achieve slime-control. Generally speaking, however, any conventional microbicide which is effective in controlling the slime has a poisonous character; furthermore it must be maintained at a specific degree of concentration for effective slime-control. Germicidal control has ordinarily been conducted by pouring microbicides into water at periodic intervals, for economic reasons. Processes in the prior art, however, have allowed the formation of slime due to proliferation of microbes in water with the lowering of concentration of a microbicide in the intervals between successive introductions thereof.

The applicants, taking the viewpoint that a more positive treatment is necessary to deal with the problems due to slime and that the most effective method of doing this would be to provide means for reducing the adhesiveness of microbial groups by use of a chemical agent, have conducted a series of investigations to reach the present invention.

On the surfaces of the micro-organisms or aggregations thereof (floc) found in some industrial waters, there exists a sticky substance having the property of adhering onto solid surfaces, and this substance constitutes the cause of the problems caused by slimes. Accordingly if this sticky substance on the surfaces of micro-organisms is denatured or removed by means of treatment with some chemical agent or other to thereby remove its adherent pro-

perty, the formation of slime will be prevented without taking the trouble to exterminate those micro-organisms *per se*.

We have found that the combined addition of certain selected chelating agents and a cationic surface active agent shows a high slime-controlling effect. The effect of this combination in slime-control has proved far superior, by virtue of a synergistic effect, to the sum of the effects exhibited by the individual compounds used separately.

The invention provides a method of treating water, especially feed water for industrial plant, to prevent or reduce the deposition of microbial slime on surfaces over which the water passes, which comprises adding to the water one of the chelating agents referred to below and a cationic surface active agent. The invention includes compositions, for addition to the water, containing both the chelating agent and the surface active agent.

The use of this method, preferably using 5 to 10%, and especially about 10%, of chelating agent with 5 to 10% of cationic surface active agent, based on the weight of microbial floc in the water, has a powerful slime-controlling effect. It is noted that this concentration is indeed lower than the concentration which would be required for obviously reducing the number of micro-organisms in the water, yet by maintaining the concentrations of the compounds added to this extent, slime formation is controlled.

The cationic surface active agent has hitherto been utilized also as a slime-controlling agent in virtue of germicidal properties on account of its strong sterilizing power, but the concentration of this cationic surface active agent preferably employed in the present invention is so far below the concentration necessary for extermination of microbes in water that it is hardly effective in killing micro-

organisms. Moreover, the chelating agent alone does not display any microbial effect in the concentration preferably employed for the present invention, either. As will be understood from the foregoing, the slime-controlling effect demonstrated by the composition under the present invention is thought to be attributable to the action of the composition which functions to extract sticky substances such as polysaccharide, protein and the like from the surface of the micro-organisms to thereby deprive them of adherent properties, but not to the microbicidal power of the compound.

The chelating agents which are used are selected from ethylenediaminetetraacetates, 1,2 - cyclohexanediaminetetraacetates, diethylene-triamine-pentacetates, and ethylenediamine - N,N' - diacetate N,N'-dipropionates.

Examples of the cationic surface active agent, are quarternary ammonium based type cationic surface active agents i.e. lauryldimethylbenzylammoniumchloride (bromide), tetradecylmethylbenzylammoniumchloride (bromide), cetyldimethylbenzylammoniumchloride (bromide), lauryltrimethylammoniumchloride (bromide) and cetyltrimethylammoniumchloride (bromide), and also pyridinium based type cationic surface active agents i.e. laurylpyridiniumchloride (bromide) and cetylpridiniumchloride (bromide).

The chemical compositions of the present invention demonstrate a powerful and excellent slime-controlling effect which is far superior to any conventional chemical agent, of which we are aware. This is shown by the following Example, which shows the effect of using a slime-controlling composition according to the present invention.

EXAMPLE

Experiments were conducted on a model plant of a circulating cooling-water system having a scale as follows:—

85	Volume of hold water	1.3 ton
	Volume of recirculating water	1.0 ton/hour
	Volume of make up water	30 litres/hour
	Temperature of heat-transfer medium	40°C.
90	Temperature of water fed to heat exchanger	20—22°C.
	Temperature of water returning from heat exchanger	31—32°C.
	Flow rate within heat exchanger	0.3cm/sec
95	Total heating surface area	1.05m ²

In order to carry out the experiments on the above cooling-water system in a short space of time, fresh activated sludge obtained from sewage was suspended in water to provide the microbial aggregations. The heat treated water was then employed as make up water, and the volume of suspended matter within the circu-

lating water was adjusted to be 200 ppm.

After adding disodium ethylenediaminetetraacetate (EDTA) as the chelating agent, and lauryldimethylbenzylammoniumchloride as the cationic surface active agent to the circulating water adjusted as above, the cooling-water system was put in operation for 7 days.

Subsequently, slime was collected from a prescribed portion of the heat exchanger by means of washing.

Similar tests for comparison purposes were also carried out using chelating agent only, cationic surface active agent only, and with neither chelating or surface active agent.

Each batch of slime thus collected was weighed after drying and the results were com-

pared, the amount of slime which adhered when the recirculating water included no chelating or surface active agent being the basis for comparison. The results of examination of the respective slime-controlling effects, in terms of percentage (%) against the comparison amount of slime (hereinafter referred to as 'adhesion ratio') when no agent was used are shown in the following Table 1:—

TABLE 1

Slime-controlling agent / Item	Concentration of slime-controlling agent (ppm)		Adhesion ratio (%) (EDTA)
None (for control)	0		100
Chelating agent only (for comparison)	10		72.0
	20		30.8
	40		28.5
Compositions of the invention	Chelating agent	Cation field-activator	Adhesion ratio (%)
	10	10	8.6
	20	10	6.5
	20	20	16.0
Cation surface active agent only (for comparison)	10		
	20		
	40		

In the light of the above findings, it is obvious that when a chelating agent or a cationic surface active agent is used independently, either one of those agents may display a slime-controlling effect on the microbial aggregations in water to some extent at about 10% concentration, but when a composition is used containing 5—10% of chelating agent and also 5—10% of cationic surface active agent, the slime-controlling effect demonstrated thereby is far better than when any one of the agents is employed individually. Especially good results have been obtained with compositions containing 5—10% of chelating agent and 5% of cationic surface active agent. In this connection, it may be noted that when the

composition of the invention was added as in the present example, there was no indication of a decrease in the number of living microbes in the water.

Further, a series of chemical analyses conducted on the slime formed within the heat exchanger used in this Example led to the findings that all the slimes formed had a composition similar to that of the activated sludge employed in the tests. By way of example, the chemical composition of the slime formed when 10 ppm of a chelating agent and 10 ppm of a cationic surface active agent were employed for the experiment is shown in the following Table 2, with reference to the slime for comparison.

TABLE 2

Item of analysis Sample	Chemical analysis	
	Organic matter	Ash (inorganic matter)
Activated sludge	72.4%	27.6%
Slime	70.8%	29.2%

WHAT WE CLAIM IS:—

1. A method of treating water to prevent or reduce the deposition of microbial slime therefrom on surfaces, which comprises adding to the water a chelating agent selected from ethylenediamine tetra-acetate, 1,2 - cyclohexanediamine tetra-acetates, diethylene-tri-amine penta-acetates and ethylenediamine-N,N' - diacetate - N,N' - dipropionates and also a cationic surface active agent.
2. A method according to claim 1, wherein the chelating agent is disodium ethylenediamine tetra-acetate.
3. A method according to claim 1 or claim 2, wherein the surface active agent is a quarternary ammonium compound.
4. A method according to any of claims 1 to 3, wherein the chelating agent is added in the proportion of 5% to 10% by weight of the microbial floc in the water.
5. A method according to any of claims 1 to 3, wherein the chelating agent is added in the proportion of about 10% by weight of the microbial floc in the water.
6. A method according to any of claims 1 to 5, wherein the cationic surface agent is

added in the proportion of 5% to 10% of the weight of microbial floc in the water.

7. A composition for addition to water to prevent or reduce the deposition of microbial slime therefrom on surfaces, which comprises a chelating agent and a cationic surface active agent, both as defined in claim 1.

8. A composition according to claim 7, wherein the chelating agent is as defined in claim 2.

9. A composition according to claim 7 or claim 8 wherein the surface active agent is as defined in claim 3.

10. A composition according to claim 7, substantially as described in the Example.

11. A method of treating water according to claim 1, substantially as hereinbefore described.

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2. A method according to claim 1, wherein the chelating agent is disodium ethylenediamine tetra-acetate.
3. A method according to claim 1 or claim 2, wherein the surface active agent is a quarternary ammonium compound.
4. A method according to any of claims 1 to 3, wherein the chelating agent is added in the proportion of 5% to 10% by weight of the microbial floc in the water.
5. A method according to any of claims 1 to 3, wherein the chelating agent is added in the proportion of about 10% by weight of the microbial floc in the water.
6. A method according to any of claims 1 to 5, wherein the cationic surface agent is

added in the proportion of 5% to 10% of the weight of microbial floc in the water.

7. A composition for addition to water to prevent or reduce the deposition of microbial slime therefrom on surfaces, which comprises a chelating agent and a cationic surface active agent, both as defined in claim 1.

8. A composition according to claim 7, wherein the chelating agent is as defined in claim 2.

9. A composition according to claim 7 or claim 8 wherein the surface active agent is as defined in claim 3.

10. A composition according to claim 7, substantially as described in the Example.

11. A method of treating water according to claim 1, substantially as hereinbefore described.

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