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(54) **Title:** PACKING ELEMENTS FOR EVAPORATIVE COOLERS WITH RESISTANCE TO BIOFILM FORMATION

(57) **Abstract:** Disclosed is a polyvinyl chloride packing material for evaporative coolers, which packing material has incorporated therein an amount effective to prevent biofilm formation of one or more antimicrobials selected from the group consisting of the metal containing zeolites and the supported metals, where the metal of the metal containing zeolites is silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, zirconium or a combination of two or more of these metals and where in the supported metals the metal is silver, a silver compound a silver complex or a combination of silver with copper, zinc or zirconium and where the support is SiO_2, TiO_2 or glass.

Packing Elements for Evaporative Coolers with Resistance to Biofilm Formation

This application claims benefit of U.S. provisional app. No. 60/852,826, filed October 19, 2006, the contents of which are hereby incorporated by reference.

This invention relates to plastic polyvinyl chloride packing for evaporative coolers, for example water cooling towers. The polyvinyl chloride packing exhibits outstanding resistance to biofilm formation.

A wide variety of industries use water as the coolant for heat transfer processes. A significant quantity of cooling water is used annually by both electrical power plants and manufacturing operations. Typical water cooled heat transfer processes include condensers and chillers. In general, the spent water is recycled to lessen both the economic and environmental impact of these heat transfer processes. This recycling requires the spent water to be cooled back to ambient temperature or slightly below, commonly by means such as a cooling tower. In general, cooling towers allow the spent water to release heat to the ambient air by cascading the spent water down an open air tower.

The packing material for use in the cooling towers comprises a suitable inert material arranged to present as large as possible a surface area to contact the gas and liquid flowing therepast. Such packing material may comprise, for example, a supported mass of irregular or regular shaped pieces, offering a large surface area to bulk ratio, over and through which the gas and liquid are cause to flow in counter current. The packing may take the form of a number of rigid grid-like structures arranged in superimposed spaced relation to one another, which arrangement is designed to break up and distribute the liquid falling freely through the tower so that maximum contact is established with the gas flowing upwardly through the tower and optimum cooling is achieved.

Packing materials are comprised of for example metal, wood or plastic such as polyvinyl chloride.

The packings surfaces are subject to fouling by microbe contamination. In particular, the surfaces are subject to a type of fouling known as biofilm formation. “Biofilm” means a mucilaginous community of mocroorgainisms such as, for example bacteria, archaea, fungi, molds, algae or protozoa.

Biofilm formation on evaporative cooler packing surfaces can result in a loss of heat exchange performance or corrosion of the surface. Biofilm formation also provides for a tacky surface on which minerals can readily deposit.

There remains a need for polyvinyl chloride packing material that is resistant to biofilm formation.

Packings for water cooling towers are disclosed in for example U.S. Pat. No. 4,762,650.

Packing, or contact packing, for cooling towers is also disclosed in U.S. Pat. No. 4,105,724.

U.S. Pat. No. 4,361,426 teaches packing, or fill, for cooling towers. The fill has a high surface area.

U.S. Pat. Nos. 6,071,542, 4,938,955, 4,775,585, 4,911,899 and 4,911,898 are aimed at resins containing antimicrobial metal containing zeolites.

U.S. Pat. No. 6,585,989 teaches metal containing zeolites and supported on silicon dioxide, titanium dioxide or glass.

Published U.S. app. No. 2004/0082492 is aimed at biocide-containing plastics internal elements in gas humidifiers, gas scrubbers or exhaust air scrubbers.

It has been found that polyvinyl chloride packing materials that have incorporated therein antimicrobial metal containing zeolites or supported silver compounds are especially resistant to biofilm formation. The polyvinyl chloride packings exhibit good visual appearance and good heat exchange performance over a long period of time.

Disclosed is a polyvinyl chloride packing material for evaporative coolers,

which packing material has incorporated therein an amount effective to prevent biofilm formation of one or more antimicrobials selected from the group consisting of the metal containing zeolites and the supported metals,

where the metal of the metal containing zeolites is silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, zirconium or a combination of two or more of these metals and

where in the supported metals the metal is silver, a silver compound a silver complex or a combination of silver with copper, zinc or zirconium and where the support is SiO_2, TiO_2 or glass.

Evaporative coolers may be used for cooling a gas such as air using a liquid such as water as a coolant, or for cooling a liquid using a gas as a coolant, and/or for humidifying a gas. Included are water cooling towers, exhaust air scrubbers, flue gas scrubbers or humidifiers of process gases. Each of these systems according to this invention employ polyvinyl chloride packing.

Such coolers are disclosed for example in U.S. Pat. Nos. 4,762,650, 4,297,224, 4,361,426 and 6,649,065 and in published U.S. app. No. 2004/0082492, the disclosures of which are hereby incorporated by reference. The coolers of this invention are in particular water cooling towers. Where the cooling towers of the cited art employ a different packing material, for example wood or metal, the present invention would substitute polyvinyl chloride.

The polyvinyl chloride packing material, also known as fill, is disclosed for example in U.S. Pat. Nos. 4,105,724, 4,361,426 and 4,311,593, the disclosures of which are hereby incorporated by reference. The polyvinyl chloride (PVC) packing may be in the form of blocks or bundles, for example corrugated PVC assembled into self supporting modules. The PVC packing may be in the form of cellular material. The PVC packing has a large surface area upon which biofilm may form.

A biofilm is a type of fouling that occurs when microorganisms attach to surfaces and secrete a hydrated polymeric matrix that surrounds them. The microorganisms in a biofilm

grow in a protected environment that insulates them from antimicrobial agents. A biofilm may be formed from lower plant life, for example algae, bacteria or fungi. A biofilm may damage PVC packing material in an evaporative cooler. Cooling water systems are excellent places for the incubation and growth of biological organisms because such systems contain nutrients from air drawn into the system and from organic materials naturally occurring in the water. Further, the water temperature is warm enough to prove an ideal incubation environment.

Biofilm formation may cause problems with water and air flow, oil fouling, mineral deposition and/or microbiological fouling.

The damage cause by a biofilm may be measured as disclosed in U.S. Pat. No. 4,297,224. For example, it may be measured by appearance, microorganism count, microscopic analysis or by heat transfer. Heat transfer, or temperature differential, across a cooling tower or heat exchanger quickly defines the existence of fouling problems where a noticeable reduction in heat transfer is observed.

The metal containing zeolites are disclosed in for example in U.S. Pat. Nos. 6,585,989, 6,071,542, 4,911,899, 4,775,585, 4,938,955 and 4,911,898, the disclosures of which are hereby incorporated by reference.

A zeolite is generally aluminosilicate having a three dimensional grown skeleton structure and is generally represented by $xM_{2/n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot zH_2O$, written with Al_2O_3 as a basis, wherein M represents an ion-exchangeable metal ion, which is usually the ion of a monovalent or divalent metal; n corresponds to the valence of the metal; x is a coefficient of the metal oxide; y is a coefficient of silica; and z is the number of water of crystallization. The zeolites of the present invention have a specific surface area of at least $150 m^2/g$.

Antimicrobial metals for use in the metal containing zeolites include silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, zirconium or a combination of two or more of these metals. Preference is given to silver, copper, zinc and zirconium or a combination of these. Especially preferred metals are silver alone or a combination of silver with copper, zinc or zirconium.

The present metal containing zeolites include surface modified metal containing zeolites according to U.S. Pat. No. 6,071,542.

The supported metals are supported on SiO_2, TiO_2 or glass. The metal in this instance is silver, a silver compound a silver complex or a combination of silver with copper, zinc or zirconium. Included within silver compounds or silver complexes are colloidal silver, silver nitrate, silver sulphate and silver chloride.

A preferred support is glass.

The present metal containing zeolite or supported metal antimicrobials are present in the PVC at a level of from about 0.01% to about 10% by weight, based on the weight of the PVC. For instance, the present antimicrobials are present from about 0.05% to about 5% by weight, or from about 0.1% to about 3% by weight, based on the weight of the PVC.

The present metal containing zeolite or supported metal antimicrobials are incorporated into the PVC packing for example prior to its formation into the final article, for example via melt blending. The antimicrobial additives are incorporated into the PVC for example during melt extrusion.

The antimicrobials may be dry mixed with PVC in the form of a powder or may be wet mixed in the form of solutions or suspensions. The antimicrobials may be incorporated into the PVC before or after molding or also by applying a dissolved or dispersed mixture to the plastic material, with or without subsequent evaporation of the solvent. The antimicrobials may be added to the PVC in the form of a masterbatch which contains the additives in a concentration of for example about 2% to about 70% by weight. In such operations, the polymer can be used in the form of powder, granules, solutions, suspensions or in the form of lattices. The antimicrobials can be added before, during or after polymerization.

The following examples illustrate the invention.

Example 1 Oil Refinery Cooling Tower

Cooling tower contained volume: 590,500 liters (156,000 gallons); circulation rate: 15,142 liters/minute (4,000 gpm); nominal cooling capacity: 12,700,000 Kcal/hr (4,200 tons); blow down: 102 liters/minute (27 gpm).

This tower contains PVC packing. The packing contains a present metal containing zeolite or a present supported metal. After operation for an extended period, the PVC packing is visually clean and free of biofilm formation.

Example 2 Packaged Cooling Towers

Two packaged cooling towers are connected in parallel to provide the following system: contained volume: 37,800 liters (10,000 gallons); circulation rate: 7,600, liters/minute (2,000 gpm); nominal cooling capacity: 2,420,000 Kcal/hr (800 tons); blow down: 344 liters/minute (91 gpm).

The packing without a present antimicrobial additive are badly fouled with biofilm. The efficiency of the tower is significantly impacted, requiring replacement of the packing. When the PVC packing contains a present metal containing zeolite or a present supported metal additive, the packing remains clear of biofilm formation.

Example 3 PVC Packing

Standard PVC packing is prepared. Control sample contains no antimicrobial additive. Test sample contains 1% by weight of a mixture of silver supported on glass and zinc supported on zeolite. The antimicrobial mixture is melt blended with the PVC.

The control and test samples of packing are arranged side by side in a standard water cooling tower. Weight gain is measured for the packing materials on a monthly basis. After 12 months, the control sample gains 20% weight. The test sample exhibits no weight gain after 12 months.

Example 4 Antimicrobial Efficacy

PVC samples are prepared. The control sample contains no antimicrobial additive. The test sample contains 1% by weight of a mixture of silver supported on glass and zinc supported on zeolite. The antimicrobial mixture is melt blended with the PVC.

The samples are treated with *methicillin resistant staphylococcus aureus* (MRSA) and tested according to JIS Z 2801.

The samples are treated with *leigonella pneumophila* and also tested according to JIS Z 2801.

The samples are inoculated with the bacteria, covered with film and kept at 35°C for 24 hours. The number of viable cells of bacteria are counted. Antimicrobial activity is calculated according to R = log B/C where R = antimicrobial activity, B = average of the number of bacteria on the control samples after incuabation for 24 hours and C = average of the number of bacteria on the test samples after incubation for 24 hours.

Results are below. Antimicrobial activity R greater than 2.0 is judged to be efficacious.

Antimicrobial efficacy against *methicillin resistant staphylococcus aureus* (MRSA)

sample	bacteria count after incubation	antimicrobial activity (R)
control	6.4 E5	
test	<10	4.8

Antimicrobial efficacy against *legionella pneumophila*

sample	bacteria count after incubation	antimicrobial activity (R)
control	5.7 E5	
test	<100	>5

What is claimed is:

1. A polyvinyl chloride packing material for evaporative coolers,

which packing material has incorporated therein an amount effective to prevent biofilm formation of one or more antimicrobials selected from the group consisting of the metal containing zeolites and the supported metals,

where the metal of the metal containing zeolites is silver, copper, zinc, mercury, tin, lead, bismuth, cadmium, chromium, cobalt, nickel, zirconium or a combination of two or more of these metals and

where in the supported metals the metal is silver, a silver compound a silver complex or a combination of silver with copper, zinc or zirconium and where the support is SiO_2, TiO_2 or glass.

2. A polyvinyl chloride packing material according to claim **1** where the antimicrobials are present from about 0.05% to about 5% by weight, based on the weight of the polyvinyl chloride.

3. A polyvinyl chloride packing material according to claim **1** where the antimicrobials are present from about 0.1% to about 3% by weight, based on the weight of the polyvinyl chloride.

4. A polyvinyl chloride packing material according to claim **1** where the antimicrobials are selected from the group consisting of the metal containing zeolites.

5. A polyvinyl chloride packing material according to claim **4** where the metal is silver, copper, zinc, zirconium or a combination thereof.

6. A polyvinyl chloride packing material according to claim **4** where the metal is silver or is a combination of silver with copper, zinc or zirconium.

7. A polyvinyl chloride packing material according to claim **1** where the antimicrobials are selected from the group consisting of the supported metals.

8. A polyvinyl chloride packing material according to claim **7** where the metal is silver or is a combination of silver with copper, zinc or zirconium.

9. A polyvinyl chloride packing material according to claim **7** where the support is glass.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/060755

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K9/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 00/52088 A (HEALTHSHIELD TECHNOLOGIES L L [US]) 8 September 2000 (2000-09-08)	1-9
Y	abstract; claims 1-19 pages 2,3	1-9
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/060755

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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