

S P E C I F I C A T I O N

Method for Preventing Deterioration of Concrete,
Mortar or High Polymer MaterialFIELD OF ART:

5 The present invention relates to a method for
preventing deterioration of concrete, mortar or a high polymer
material, and more particularly to a method for preventing
deterioration of concrete, mortar or a high polymer material
caused by sulfur-oxidizing bacteria of a genus of Thiobacillus
10 especially in sewage-treating facilities and the like.

BACKGROUND ART:

 It has been known that deterioration takes place by
the action of hydrogen sulfide evolved in sewage-treating
facilities or the like in such manner that the concrete or
15 mortar structures tend to become gypsiferous or a paint is
peeled off therefrom or cracks are formed in a high polymer
material such as polyester. Such deterioration is supposed to
be ascribable to oxidation of hydrogen sulfide to sulfuric
acid by the action of sulfur-oxidizing bacteria of a genus of
20 Thiobacillus which generally lives widely in soil or water and
grows with assimilation of carbon dioxide by oxidation of
sulfur compounds, and a variety of methods have been proposed
for preventing the deterioration. These preventative methods
are roughly classified into the following four methods; (1) a
25 method for inhibiting the formation of sulfides, (2) a method
for inhibiting the generation of hydrogen sulfide, (3) a



method for inhibiting the formation of sulfuric acid from hydrogen sulfide, and (4) a method for using anti-corrosive materials.

As the above method (1) or (2), there is known a method wherein hydrogen peroxide or chlorine compounds, or metallic salts such as iron, zinc, lead, copper, etc. is added in a large amount to sewage, as advocated by US Environmental Protection Agency. However, this method involves problems for economical reasons. As the method (3), there is known a method wherein ventilation is performed to reduce the concentration of hydrogen sulfide in the air. However, this method permits emission of bad odor and still fails to obtain a satisfactory result in the present status. What is more, a method wherein glass fibers and stainless steel, for example, are utilized as the anti-corrosive material is known as the method (4), but this method has a drawback in that problems arise in facilitated construction and in economy.

There are also known organic compounds such as Na-PCP as a bacteriostatic agent to be incorporated into sulfur mortar. However, the use of these compounds permits the formation of pinholes and cracks in concrete or mortar, thus involving a problem of being devoid of durability. In addition, the use of the above Na-PCP is prohibited at present.

It is an object of the present invention to provide a method capable of preventing deterioration of concrete,

mortar or a high polymer material efficiently and for an extended period of time.

BRIEF DESCRIPTION OF THE DRAWINGS:

Fig. 1a is a photograph showing the state of deterioration of the surface of a test sample which is used in Example 1.

Fig. 1b is an explanatory diagram for explaining Fig. 1a.

Fig. 2a is a photograph showing the state of deterioration of the surface of a test sample which is used in Example 2.

Fig. 2b is an explanatory diagram for explaining Fig. 2a.

Fig. 3 is a schematic diagram showing a deterioration-accelerating system used in Examples 2-4.

DISCLOSURE OF THE INVENTION:

In accordance with the present invention, there is provided a method for preventing deterioration of concrete, mortar or a high polymer material, characterized in that a metal selected from the group consisting of nickel, a nickel oxide, Raney nickel, stabilized nickel, tin, a tin oxide, a cobalt oxide, stainless steel and mixtures thereof is incorporated into the concrete, the mortar or the high polymer material.

THE BEST MODE FOR CARRYING OUT THE INVENTION:

The present invention is explained further in detail



hereinbelow.

The method of the present invention is characterized by incorporating a specific metal into concrete, mortar or a high polymer material for exhibiting a bacteriostatic and/or bactericidal effect to sulfur-oxidizing bacteria of a genus of Thiobacillus propagating in soil, water and the like which is usually supposed to cause deterioration of concrete, mortar or a high polymer material.

The above metal is a component which is reacted with sulfuric acid generated at the time of deterioration of concrete, mortar or a high polymer material by the action of sulfur-oxidizing bacteria of a genus of Thiobacillus to form a sulfate, thus exhibiting bacteriostatic and/or bactericidal effect to the sulfur-oxidizing bacteria, and more particularly can be selected from the group consisting of nickel, a nickel oxide, Raney nickel, a stabilized nickel, tin, a tin oxide, a cobalt oxide, stainless steel and mixtures thereof.

The above metal is desirably in the form of fine powders so as to be mixed easily and homogeneously with concrete, mortar or a high polymer material, and more preferably of finely divided powders having an average particle diameter of 0.001-0.1 mm. The proportion of the above metal to be incorporated is preferably 0.001-25 parts by weight, more preferably 0.1-20 parts by weight per 100 parts by weight of the cement ingredient in concrete or mortar or of the high polymer material. If the proportion is less than



0.001 part by weight, it is difficult to maintain the bacteriostatic and bactericidal effects against the sulfur-oxidizing bacteria for an extended period of time, whereas if the proportion exceeds 25 parts by weight, no enhancement can not be expected in bacteriostatic and bactericidal effects against the sulfur-oxidizing bacteria, and moreover, a problem arises in regard to cost, thus being not preferred.

The method of this invention can be carried out by admixing known concrete, mortar or a high polymer material such as polyethylene, polyester, polyvinyl chloride, epoxy resin or a known paint composition with the above metal and then forming concrete, mortar or the high polymer material in a desired place according to a usual method.

The method of the present invention wherein the specific metal is used for exhibiting bacteriostatic or bactericidal effect to the sulfur-oxidizing bacteria can prevent deterioration of concrete, mortar or a high polymer material efficiently and for a long period of time. Thus, the method of the present invention is extremely useful for preventing deterioration of concrete, mortar or a high polymer material in sewage treatment facilities and the like where such material is brought into contact with water.

EXAMPLES

The present invention will now be illustrated in more detail by way of Examples and Comparative Examples. However, the present invention is not limited thereto.



Example 1

To a mortar composition composed of 10 parts by weight of cement, 200 parts by weight of sand and 50 parts by weight of water were added finely divided powders of nickel, a nickel oxide, tin, a tin oxide or stainless steel (SUS 304) of not more than 200 mesh individually in amounts of 2, 10 and 20 parts by weight, respectively, and each mixture was well mixed under agitation by the aid of a mortar mixer and molded in the shape of 4 x 4 x 16 cm, respectively, to form 15 pieces of mortar test samples. The resultant mortar test samples were exposed in an aerial portion of sludge facilities in a sewage treatment plant. After exposing the test samples in sludge for 2 years after the placement, terminal end portions of each test sample were cut off by 4 cm to investigate the deterioration state by observing their cut out areas and the surface condition of the test samples. Table 1 shows a result of the cut out area of the test samples, Fig. 1a is a photograph showing the surface condition of the test samples, and Fig. 1b is an explanatory diagram of Fig. 1a.

Comparative Example 1

Each test was processed and carried out in the same manner as described in Example 1 except that copper or copper oxide finely divided powders, an organic compound of isophthalone series (trade name: "FINESIDE D-75"), an organic compound of imide series (trade name: "FINESIDE CP"), and a nitrogen/sulfur-containing organic compound (trade name:

"FINESIDE A-3") (all manufactured by Tokyo Fine Chemicals Co., Ltd.) each conventionally used for inhibition of microorganisms were used independently in place of the finely divided powders of nickel, nickel oxide, tin, tin oxide or stainless steel, or except that a mortar test sample made free of the finely divided powder component was used. A result of the test is also shown in Table 1 and Figs. 1a and 1b in the same manner as in Example 1.

Alternatively, Fig. 1b is an explanatory diagram for Fig. 1a and 1-29 in Fig. 1b stand for the test samples corresponding to those in Fig. 1a, respectively. More precisely, 1, 6 and 11 stand for the test samples to which the nickel finely divided powders were added, 2, 7 and 12 stand for the test samples to which the nickel oxide finely divided powders were added, 3, 8 and 13 stand for the test samples to which stainless steel finely divided powders were added, 4, 9 and 14 stand for the test samples to which the tin finely divided powders were added, 5, 10 and 15 stand for the test samples to which the tin oxide finely divided powders were added, 16, 21 and 25 stand for the test samples to which the organic compound of imide series (trade name: "FINESIDE CP"), 17 stands for the test sample to which the nitrogen/sulfur-containing organic compound (trade name: "FINESIDE A-3" was added, 18, 22 and 26 stand for the test samples to which the organic compound of isophthalone series (trade name: "FINESIDE D-75"), 19, 23 and 27 stand for the test samples to which the

copper finely divided powders were added, and 20, 24 and 28 stand for the test samples to which the copper oxide finely divided powders were added, respectively. Further, 1-5 and 16-20 stand for the test samples wherein the finely divided powder components or the like were incorporated in an amount of 2 parts by weight per 100 parts by weight of cement, 6-10 and 21-24 stand for the test samples wherein the finely divided powder components or the like were incorporated in an amount of 10 parts by weight per 100 parts by weight of cement, 11-15 and 25-28 stand for the test samples wherein the finely divided powder components or the like were incorporated in an amount of 20 parts by weight per 100 parts by weight of cement, and 29 stands for the test sample wherein the mortar component alone was used.

Table 1

	Example 1					Comparative Example 1					
	Ni	NiO	Sn	SnO	stainless steel	Cu	CuO	P-75 ¹⁾	CP ²⁾	A-3 ³⁾	No addition
Addition of 2 parts by weight	0	0	0	0	0	1430	257	46	8	23	155
Addition of 10 parts by weight	0	0	0	0	0	235	15	183	10	Not cured	1105
Addition of 20 parts by weight	0	0	0	0	0	23	8	1250	12	Not cured	126

10 in terms of mm²

1) An organic compound of isophthalone series (trade name:
"FINESIDE D-75")

2) An organic compound of imide series (trade name:
"FINESIDE CP")

15 3) A nitrogen/sulfur-containing organic compound (trade name:
"FINESIDE A-3")

All manufactured by Tokyo Fine Chemicals Co., Ltd.

Example 2

20 To a mortar composition composed of 100 parts by
weight of cement, 200 parts by weight of sand and 50 parts by
weight of water were added finely divided powders of nickel,
tin or stainless steel (SUS 304) of not more than 200 mesh, so
that each metal component was 0.1 part by weight,
respectively, and each mixture was thoroughly mixed under
agitation by the aid of a mortar mixer, and molded in the
25 shape of 4 x 4 x 16 cm, respectively, to form 3 mortar test
samples. The resultant mortar test sample were subjected to a

deterioration-accelerating system using sulfur bacteria as shown in Fig. 3 to perform a deterioration test. In this case, an analogous test was also carried out on a test sample consisting of the mortar component alone free of the above
5 finely divided powders by way of comparison. The testing method will now be explained hereinafter, with reference to Fig. 3.

In Fig. 3, 40 stands for a deterioration-accelerating system wherein 41 for a permecal permeator for
10 supplying a hydrogen sulfide gas of a constant concentration through a line 45 to a reaction tank 50. A compressed air from which any impurities have been eliminated is supplied through an active carbon column 42, a compressor 43 and an air
15 drier 44 to the permeator 41 where the compressed air is brought into contact with a liquefied hydrogen sulfide and a hydrogen gas of 75 ppm is supplied through a line 45 to the
20 reaction tank 50 maintained at 30°C. The test was carried out by accommodating each of the above mortar test samples 51 in the reaction tank 50 in the state of being dipped by 40% in
25 water, and spraying a sulfur-oxidizing bacteria of a genus of Thiobacillus to each mortar test sample from a spray 54 connected to a cultivation liquid tank 53 each time at a concentration of 10^6 cells/unit every 14 days periodically for 6 months. The cultivation liquid used had a composition of 2
g of $(\text{NH}_4)_2\text{SO}_4$, 3 g of KNO_3 , 0.5 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.25 g of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, 0.01 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.3 mg of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and



0.5 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per liter, while a commercially available sulfur-oxidizing bacterium was used. After completion of the test, the test samples were taken out from the reaction tank 50 and the same test as described in Example 1 was carried out. A result of the test is shown in Table 2 and Figs. 2a and 2b.

Alternatively, Fig. 2b is an explanatory diagram for Fig. 2a and 30-33 in Fig. 2b stand for the test samples corresponding to those in Fig. 2a, respectively. More precisely, 30, 31 and 33 stand for the test samples blended with tin finely divided powders, nickel finely divided powders and stainless steel finely divided powders, respectively, while 34 stands for the test sample wherein the mortar component alone was used.

Table 2

Ni	Sn	Stainless steel	No addition
0	0	0	35

in terms of mm^2

Example 3

Metal finely divided powders in an amount of 0.1 part by weight were respectively mixed with 100 parts by weight of an ortho-type polyester resin ("LIGOLAK 158BQT") manufactured by Showa High Polymer Co., Ltd., and each composition was molded in accordance with ASTM C-581-68.

5 The resultant molded sample was placed on two stainless steel bars of 1 cm in diameter spaced for a distance of 8 cm while a similar stainless steel bar was placed in the central part of the molded sample, and the central part of the molded sample was deformed downward by 5 mm thereby making the sample arched.

10 The molded sample was allowed to stand for 9 months in the same deterioration-accelerating system as used in Example 2 whereupon no abnormality was observed, such as cracks.

Example 4

15 Test samples were molded and tested for 6 months in the deterioration-accelerating system in the same manner as described in Example 2 except that a concrete having a nominal strength of 210 kg/m^2 was used in place of the mortar and shaped into test sample of $10 \times 10 \times 40$ cm in size. As a result, no change was observed in the test samples wherein the metals of the present invention had been incorporated. On the other hand, the test sample consisting of the concrete component free of the metal of the present invention had a cut off area of 3510 mm^2 .

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SCOPE OF THE CLAIMS:

1. A method for preventing deterioration of concrete, mortar or a high polymer material, characterized in that a metal selected from the group consisting of nickel, a nickel oxide, Raney nickel, stabilized nickel, tin, a tin oxide, a cobalt oxide, stainless steel and mixtures thereof is incorporated into the concrete, the mortar or the high polymer material.
2. A method for preventing deterioration as set forth in claim 1, wherein the metal is in the form of finely divided powders.
3. A method for preventing deterioration as set forth in claim 2, wherein an average diameter of the powders is 0.001-0.1 mm.
4. A method for preventing deterioration as set forth in claim 1, wherein a proportion of the metal is 0.0001-25 parts by weight based on 100 parts by weight of the cement component in concrete and mortar or of the high polymer material.
5. A method for preventing deterioration as set forth in claim 1, wherein the high polymer material is selected from the group consisting of polyethylene, polyester, polyvinyl chloride, an epoxy resin and mixtures thereof.



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FIG. 1a

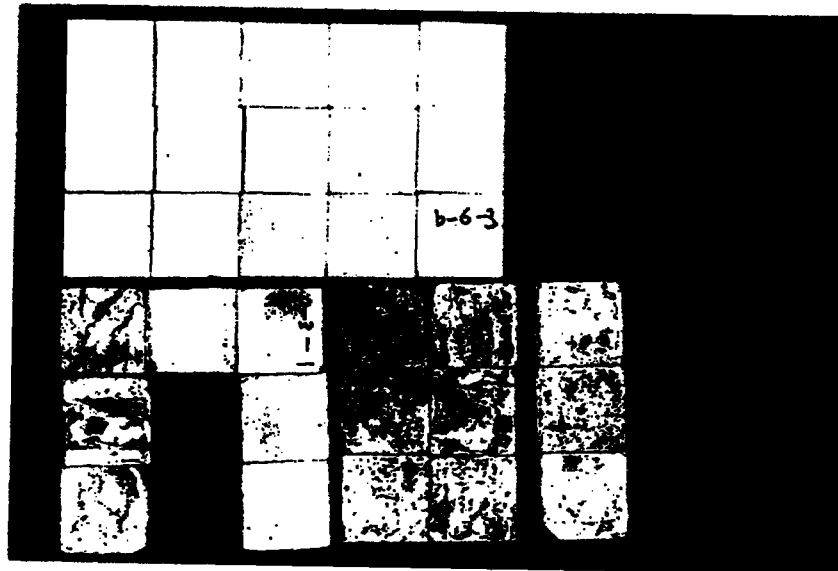


FIG. 1b

1	2	3	4	5
6	7	8	9	10
11	12	13	14	15

16	17	18	19	20
21		22	23	24
25		26	27	28

29

2/3

FIG.2a

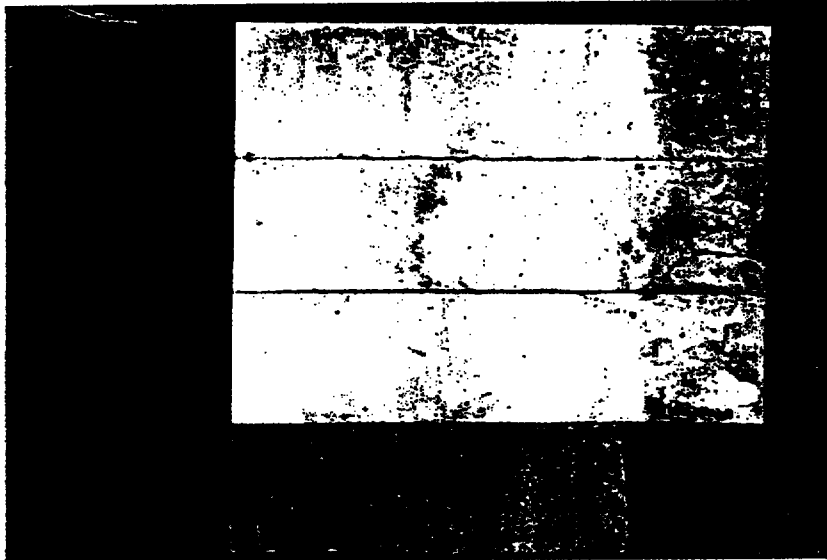
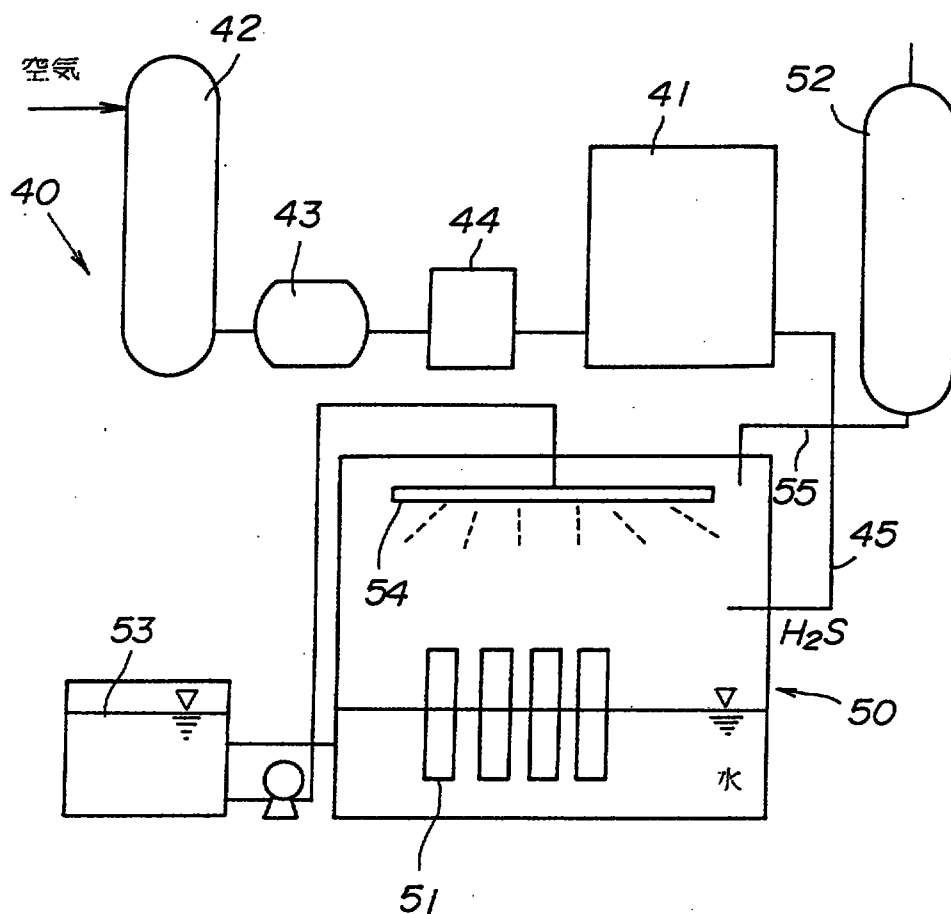


FIG.2b

30
31
32
33

3/3

FIG. 3



ABSTRACT

A method for preventing deterioration of concrete, mortar or a high polymer material is disclosed wherein a metal selected from nickel, nickel oxide, Raney nickel, stabilized nickel, tin, tin oxide, cobalt oxide, stainless steel or mixtures thereof is incorporated into concrete, mortar or a high polymer material. Deterioration of concrete, mortar or a high polymer material, especially in sewage treatment facilities and the like can be prevented by incorporating such metal thereinto.

(Fig. 1a)

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THIS SHEET HAS BEEN
REPLACED

REPLACEMENT SHEET

Date : 05 SEP 1996

Substitute Sheet - 4 September 1996

ABSTRACT

**Method for Preventing Deterioration of Concrete,
Mortar or High Polymer Material**

A method for preventing deterioration of concrete, mortar or a high polymer material is disclosed wherein a metal selected from nickel, nickel oxide, Raney nickel, stabilized nickel, tin, tin oxide, cobalt oxide, stainless steel or mixtures thereof is incorporated into concrete, mortar or a high polymer material. Deterioration of concrete, mortar or a high polymer material, especially in sewage treatment facilities and the like can be prevented by incorporating such metal thereinto.

(Please note that Figure 1A should accompany the abstract when published)

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S P E C I F I C A T I O N

Method for Preventing Deterioration of Concrete,
Mortar or ~~High~~ Polymer Material

FIELD OF ART:

5 The present invention relates to a method for
preventing deterioration of concrete, mortar or a ~~high~~ polymer
material, and more particularly to a method for preventing
deterioration of concrete, mortar or a ~~high~~ polymer material
caused by sulfur-oxidizing bacteria of a genus of Thiobacillus
10 especially in sewage-treating facilities and the like.

BACKGROUND ART:

 It has been known that deterioration takes place by
the action of hydrogen sulfide evolved in sewage-treating
facilities or the like in such manner that the concrete or
15 mortar structures tend to become gypsiferous or a paint is
peeled off therefrom or cracks are formed in a ~~high~~ polymer
material such as polyester. Such deterioration is supposed to
be ascribable to oxidation of hydrogen sulfide to sulfuric
acid by the action of sulfur-oxidizing bacteria of a genus of
20 Thiobacillus which generally lives widely in soil or water and
grows with assimilation of carbon dioxide by oxidation of
sulfur compounds, and a variety of methods have been proposed
for preventing the deterioration. These preventative methods
are roughly classified into the following four methods; (1) a
25 method for inhibiting the formation of sulfides, (2) a method
for inhibiting the generation of hydrogen sulfide, (3) a

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mortar or a polymer material efficiently and for an extended period of time.

The method of the present invention is characterised by incorporating a specific metal powder or metal oxide powder into concrete, mortar or a polymer material for exhibiting a bacteriostatic and/or bactericidal effect to sulfur-oxidising bacteria of a genus of Thiobacillus which is usually supposed to cause deterioration of concrete, mortar or a polymer material in sewage treatment works.

The above metal powder or metal oxide powder is a component which reacts with sulfuric acid generated at the time of deterioration of concrete, mortar or a polymer material by the action of sulfur-oxidising bacteria of a genus of Thiobacillus to form a sulfate, thus exhibiting bacteriostatic and/or bactericidal effect to the sulfur-oxidizing bacteria, and more particular is selected from the group consisting of powders of nickel, a nickel oxide, Raney nickel, a stabilized nickel, tin, a tin oxide, a cobalt oxide, stainless steel and mixtures thereof.

The above metal or metal oxide is in the form of powders so as to be mixed easily and homogeneously with concrete, mortar or a polymer material, and more preferably of finely divided powders have an average particle diameter of 0.001-0.1mm. The proportion of the above metal or metal oxide powder to be incorporated is preferably 0.001-25 parts by weight, more preferably 0.1-20 parts by weight per 100 parts by weight of the cement ingredient in concrete or mortar or of the polymer material. If the proportion is less than 0.001 part by weight, it is difficult to maintain the bacteriostatic and bactericidal effects against the sulfur-oxidizing bacteria for an extended period of time, whereas if the proportion exceeds 25 parts by weight, no enhancement can be expected in bacteriostatic and bactericidal effects against the sulfur-oxidizing bacteria, and moreover, a problem arises in regard to cost, thus being

not preferred.

The method of this invention can be carried out by admixing known concrete, mortar or polymer materials such as polyethylene, polyester, polyvinyl chloride, an epoxy resin or mixtures thereof (e.g. a paint composition) with the above metal or metal oxide powder then forming concrete, mortar or the polymer material in a desired place according to a usual method.

10

The method of the present invention wherein the specified metal powder or metal oxide powder is used achieves bacteriostatic or bactericidal effect to the sulfur-oxidizing bacteria that can prevent deterioration of the concrete, mortar or polymer material efficiently and for a long period of time in sewage treatment facilities where such material is brought into contact with water.

Specific embodiments of the present invention will now be described further, by way of example, with reference to the accompanying drawings, in which:-

Fig. 1a is a photograph showing the state of
5 deterioration of the surface of a test sample which is used in Example 1;

Fig. 1b is an explanatory diagram for explaining Fig.
1a;

Fig. 2a is a photograph showing the state of
10 deterioration of the surface of a test sample which is used in Example 2;

Fig. 2b is an explanatory diagram for explaining Fig.
2a; and

Fig. 3 is a schematic diagram showing a deterioration-
15 accelerating system used in Examples 2-4.

deterioration-accelerating system using sulfur bacteria as shown in Fig. 3 to perform a deterioration test. In this case, an analogous test was also carried out on a test sample consisting of the mortar component alone free of the above finely divided powders by way of comparison. The testing method will now be explained hereinafter, with reference to Fig. 3.

In Fig. 3, 40 stands for a deterioration-accelerating system wherein 41 for a permecal permeator for supplying a hydrogen sulfide gas of a constant concentration through a line 45 to a reaction tank 50. A compressed air from which any impurities have been eliminated is supplied through an active carbon column 42, a compressor 43 and an air drier 44 to the permeator 41 where the compressed air is brought into contact with a liquefied hydrogen sulfide and a hydrogen gas of 75 ppm is supplied through a line ~~45~~⁵⁵ to the reaction tank 50 maintained at 30°C. The test was carried out by accommodating each of the above mortar test samples 51 in the reaction tank 50 in the state of being dipped by 40% in water, and spraying a sulfur-oxidizing bacteria of a genus of Thiobacillus to each mortar test sample from a spray 54 connected to a cultivation liquid tank 53 each time at a concentration of 10^6 cells/unit every 14 days periodically for 6 months. The cultivation liquid used had a composition of 2 g of $(\text{NH}_4)_2\text{SO}_4$, 3 g of KNO_3 , 0.5 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 0.25 g of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, 0.01 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.3 mg of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and

Date: 06 AUG 1997

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CLAIMS

1. A method of preventing deterioration of concrete, mortar
or ^apolymer material in contact with water containing sulfide
5 compounds and sulfur oxidizing bacteria in a sewage
treatment works, characterized in that metal powders or
metal oxide powders selected from nickel powders, nickel
oxide powders, Raney nickel powders, stabilized nickel
powders, tin powders, tin oxide powders, cobalt oxide
10 powders, stainless steel powders and mixtures thereof are
incorporated into the concrete, the mortar or the polymer
material.
2. A method of preventing deterioration as set forth in
15 claim 1, wherein the average particle diameter of the
powders is 0.001-0.1mm.
3. A method of preventing deterioration as set forth in
claim 1, wherein the proportion of the metal powders or
20 metal oxide powders is 0.001-25 parts by weight based on 100
parts by weight of the cement component in concrete and
mortar or of the polymer material.
4. A method of preventing deterioration as set forth in
25 claim 1, wherein the polymer material is selected from
polyethylene, polyester, polyvinyl chloride, an epoxy resin
and mixtures thereof.



* C L M S *

ABSTRACT

Method for Preventing Deterioration of Concrete, Mortar
or Polymer Material

A method of preventing deterioration of concrete, mortar or polymer material is disclosed wherein metal powders or metal oxide powders selected from nickel powders, nickel oxide powders, Raney nickel powders, stabilized nickel powders, tin powders, tin oxide powders, cobalt oxide powders, stainless steel powders or mixtures thereof are incorporated into concrete, the mortar or the polymer material. Deterioration of concrete, the mortar or the polymer material, especially in sewage treatment facilities and the like can be prevented by incorporating such metal powders or metal oxide powders.

(Figure 1A)

FIG. 3

