

PATENT SPECIFICATION

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 RONALD ALFRED CRUMP

(54) TREATMENT OF UNDERWATER SURFACES

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of
 Britannic House, Moor Lane, London, EC2Y 9BU, a British Company, 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:—

This invention relates to a process for the treatment of underwater surfaces to
 reduce surface roughness and corrosion.

Surface roughness increases resistance to motion, thereby reducing a ship's
 speed and increasing its fuel consumption.

Surface roughness is of two types — intrinsic and extrinsic.

Intrinsic surface roughness depends on the state of the hull before painting,
 the care with which it is prepared before painting, the conditions under which the
 various layers of paint are applied, and, after a ship has been in service, the extent
 of deterioration of the paint work and the amount of corrosion which has taken
 place.

Extrinsic roughness is caused by fouling. This is an accumulative process in
 which marine organisms become attached and grow over an extended period of
 time. A fresh surface submerged in the sea becomes coated with a primary
 glycoprotein film within a matter of hours. This film acts as a substrate for bacteria
 which attach themselves by means of acidic polysaccharides. Diatoms and stalked
 protozoa become attached and grow after the bacterial film has become
 established. After longer periods of immersion two other principal types of fouling
 may be observed. The first class consists of algal growth, commonly referred to as
 weed fouling, and examples of such "weed" are Enteromorpha and Ectocarpus
 species. The second class consists of hard-shell organisms, e.g. the stalked and
 acorn varieties of barnacles.

The combined surface-roughness of these types and the amount of drag which
 this produces is a source of considerable expense to ship owners. For a speed loss
 of 1 knot, 24 days are lost per year. At 1974 charter rates this loss can be reckoned,
 in the case of a large crude oil carrier, as several hundred thousand pounds/year.

Intrinsic surface roughness can be kept down by skilled and careful
 workmanship carried out under good conditions, but even so, it cannot be
 eliminated. In many cases the paint has to be applied in adverse circumstances
 which leave a considerable degree of surface roughness.

In order to combat marine growth, an anti-fouling paint is usually applied as
 the top coat. This contains toxic materials, such as cuprous oxide, which are slowly
 leached out. The leaching process cannot be uniformly controlled and is
 undesirably rapid immediately after a vessel enters or re-enters service, with the
 result that higher concentrations of toxic material than are necessary are present
 around the ship initially, resulting in waste and pollution, and lower concentrations
 subsequently, resulting in a build up of marine growth. Furthermore, conventional

anti-fouling paints produce an electrically polarised surface which roughens with age and encourages the primary film formation mentioned above. While sufficient toxins are being exuded, bacterial growth is inhibited, but when this is no longer the case, growth is encouraged.

When marine growth occurs under these conditions, it adheres strongly to ships' hulls and is usually removed by dry-docking, scraping and re-painting, an expensive and time-consuming procedure. Alternatively, some limited improvement can be achieved by high pressure water hosing or mechanical scrubbing. However, because of the porous nature of the paint the roots of the growth are not removed, so the improvement is only transient.

Thus the ship owner is faced with the problem of choosing short but frequent, or infrequent but longer, periods while his ship is out of commission.

To avoid the problem set out above, it has been proposed to coat ship's hull with a film of wax. Thus U.K. Patent No. 1,336,103 claims a method of temporarily protecting a ship's hull after launching with a coating of wax. U.K. Patent No. 1,441,611 claims a modification of the method of 1,336,103 in which the nature, thickness and method of application of the coating render it durable enough to promise protection for at least one year. The U.K. Patent No. 1,439,773 claims a method of providing protection against fouling to a surface destined to be below water during use which comprises applying a substantially pure, durable wax layer to the surface, optionally over a paint coat, the layer being formed by spraying molten wax on to the surface (or paint coat where provided) and allowing it to harden in situ to form the layer. The sprayed layer may be smoothed by at least partially remelting it with a smoothing tool.

Practical experience with wax coatings on oil tankers and experimental results obtained from test plates immersed in sea water and from laboratory tests has confirmed the potential of wax coating but has high-lighted two important factors. These are:—

(i) that the smoothness of the wax surface is important in reducing drag and requires special care and attention.

(ii) that wax itself has no inherent anti-fouling properties.

The present invention is concerned with the incorporation of biocides in the wax.

According to the present invention, a process for coating a surface capable of underwater use with wax is characterised in that the wax coating has a thickness of from 5 to 500 micrometres and contains at least one biocide dispersed or dissolved in the wax which is effective against marine weed and/or shell growth when so dispersed or dissolved.

As indicated above, it is well known to protect underwater surfaces with anti-fouling paint, which contains toxins effective against weed and/or shell growth. Anti-fouling paint films have a degree of porosity and they are effective because the toxins are slowly leached out to give a continuous supply of toxin in the water adjacent to the paint surface. Wax films are, however, in general, impervious to water at any thickness above 5 micrometres. Experiments have shown, also, that when a wax film at least 50 micrometres thick is applied by spraying molten wax onto anti-fouling paint the toxins in the paint are effectively sealed in, do not migrate through the wax and, hence, do not reach the wax even after several months exposure to sea water.

It follows, therefore, that biocides effective when dispersed or dissolved in wax differ in type or action from conventional toxins for anti-fouling. In particular, no leaching action is required; the biocides must repel weed and shells by a simple contact mechanism. In cases where the biocide molecule, or fragments of it, enter the fouling organism, the biocides must be chosen to act rapidly and before the organism has grown to the size of which it materially increases surface roughness. This contact action must be such as to maintain the surface free from living and dead organisms for long periods without replenishment. They are preferably water-insoluble particularly in sea-water so that loss from the wax surface is minimised and should also be insoluble if they are to be used with aqueous wax dispersions.

The wax coating may have a thickness of from 50 to 300 micrometres. As indicated above, an underlying anti-fouling paint coating will be ineffective if the wax coating is at least 50 micrometres thick and is applied by spraying molten wax. An underlying anti-fouling paint may still be used, however, in case the wax coating is accidentally damaged or removed. Wax coatings below 50 micrometres e.g. 10 to 49 micrometres may also be used, in which case the biocide in the paint

may migrate slowly through the coating to augment the surface action of the toxins in the wax.

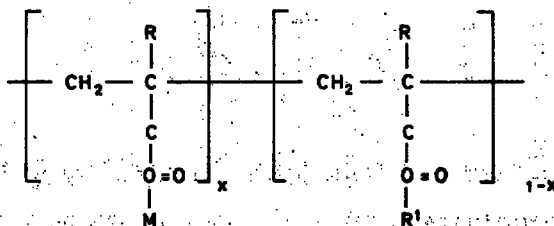
The wax coating may be applied to a surface by spraying molten wax onto the surface as described in U.K. Patent No. 1,439,773 or by applying an aqueous dispersion of a wax as described in U.K. Patent Application No. 11189/74 (Serial No. 1,479,701). With either method the biocides are soluble or easily dispersed in molten wax. They are preferably thermally stable up to at least 150°C, or up to at least 80°C in the case of wax dispersions. This thermal stability is obviously desirable when molten wax is sprayed onto the surface and is desirable also when an aqueous dispersion is used to facilitate the incorporation of the biocide in the dispersion.

Effective biocides may be of two types, metal salts and organic compounds having biocidally active molecular structures containing S, Cl, N or, in some cases, O. Each type may be further subdivided into known biocides selected for their effectiveness in wax and compounds not previously known as biocides.

In the metal salts, the metal cation may be copper, zinc, nickel, cobalt or manganese. Tin may be used but is not preferred. The acid anion is preferably derived from an organic acid to confer solubility in wax. Suitable acids may be alkyl, alkenyl or aryl carboxylic acids having from 2 to 100 carbon atoms. Another class of acids may be polymeric acids having an average molecular weight of from 200 to 500,000, e.g. polyacrylic acid.

Preferred salts may be copper or cobalt naphthenates, zinc stearate, nickel or manganese acetyl-acetonates (which have limited solubility in wax but which are readily dispersable in molten wax) and Cu, Zn, Ni, and Sn polyacrylates.

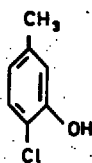
The metal polyacrylates may have the following general formula



where R is H, or C₁—C₄ alkyl, R' is H or C₁—C₃₀ hydrocarbyl, M is a metal cation as defined above and x is such as to give from 5 to 50 molar % of metal in the polymer. The two structures may be randomly positioned in the polymer and when M is a polyvalent metal cation there will be additional cross-linking through the metal cation.

Preferred organic compounds containing S, Cl or N or combinations of these elements include the following examples, in which a cyclic structure is often beneficial:—

(a) 4-chloro-m-cresol



(b) p-dichloro-benzene

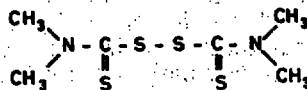


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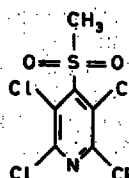
(c) tetramethylthiuram disulphide
(thiram)



sold under the Registered Trade Mark "Nomersan" by Plant Protection Ltd.

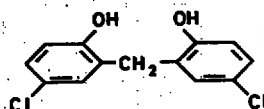
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(d) 2,3,5,6-tetra-chloro-4-
(methyl-sulphonyl) pyridine



sold under the Registered Trade Mark "Dowicil" S13 by Dow Chemical Co. Ltd.

(e) the pesticide known as dichlorophen

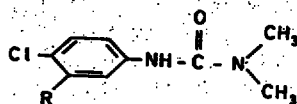


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sold under the Registered Trade Mark "Panacide" by BDH Ltd.

(f) phenyl-dimethyl urea known as (diuron and monuron)



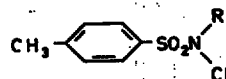
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where R = H or Cl

sold under the Registered Trade Marks "Karmet" and "Telvar" by DuPont

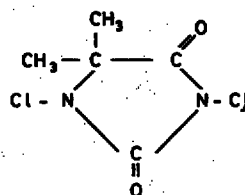
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(g) (di)-chloramine-T



where R = H or Cl

(h) 2,4-dichloro-5,5-dimethylhydantoin

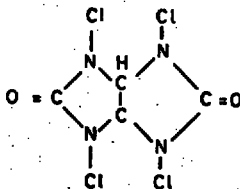


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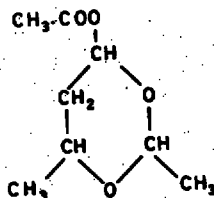
sold under the Registered Trade Mark "Halane" by BASF.

(i) tetrachloroglycoluril



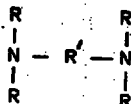
supplied by Diamond Chemicals.

In addition several type of oxygen-containing compounds are effective contact biocides. Phenols and bisphenols give satisfactory activity but must be chosen with care to ensure low values of water solubility and volatility. A particularly useful oxygen compound is the cyclic acetal, 6-acetoxy-2,4-dimethyl-m-dioxane



sold under the Registered Trade Mark Givgard DXN by Givaudan Ltd. Also effective are the polyionenes.

Polyionenes are polymers having positively charged nitrogen atoms in their backbone. They may be prepared by reacting diamines of general formula

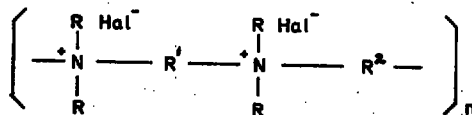


with dihalides of general formula



where R may be the same or different saturated or unsaturated alkyl, cyclo-alkyl or aryl groups, with from 1—100 C atoms, preferably C_1 — C_{30} , and preferably aliphatic groups, and R^1 and R^2 are as for R apart from having one less H atom.

The polymers have the general structure



where n preferably gives polymers of at least 1500 average molecular weight. In one specific case N,N,N',N' -tetramethyl ethylene diamine may be reacted with hexane-1,6-dibromide.

The halogen may be Br, I, Cl or F, Br being preferred for the initial preparation. The halogen may, however, be exchanged by treating the ionene with a known halogen-exchange material, e.g. a Br-ionene can be converted to an I-ionene by treatment with an aqueous solution of KI/I_2 . The halogen used may affect the water-solubility, a Br-ionene from N,N,N',N' tetra-methyl ethylene

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diamine and hexane-1,6-dibromide being water-soluble, for example, while the corresponding I-ionene is water-insoluble.

The amount of biocide may be from 1 to 70% wt, more particularly 1 to 40% wt by weight of wax. As previously indicated only the biocides at the wax surface confers anti-fouling activity but the biocide is preferably uniformly dispersed through the wax coating to allow for wear of the coating.

Where individual biocides have been shown to exhibit particularly successful activity against a given form of fouling, e.g. weed growth, they may be combined with other biocides to given protection against a wider range of fouling organisms.

In preferred method of use a wax coating may be lightly scrubbed periodically, preferably under water and without dry-docking the coated ship, so that fresh biocidally active surfaces may be produced.

A wide range of waxes may be used, but the wax preferably has a melting point of from 45 to 120°C and penetration value of from 1 to 60 mm x 10 by the method of ASTM D.1321. Suitable waxes include mineral waxes, e.g. paraffin wax, chlorinated paraffin wax, microcrystalline wax, slack wax, ozokerite and ceresine, vegetable or animal waxes, e.g. carnauba wax, and synthetic waxes, e.g. Fischer-Tropsch wax. Both oxidised and unoxidised waxes may be used.

The wax, whether applied by hot spraying or as an aqueous dispersion, may also contain from 1 to 20% wt of the wax of an alkyd or shellac resin to assist in conferring high surface gloss on the coating. Alternatively, polyethylene or polyvinyl acetate may be added for this purpose.

The present invention includes surfaces intended for under-water use having a wax coating containing a biocide effective against weed and/or shell growth when dispersed or dissolved in the wax.

The surfaces may be ships' hulls or other fixed or moveable underwater surfaces, e.g. the legs of offshore drilling rigs and production platforms.

The invention is illustrated by the following Examples.

Examples 1—12.

Film-forming compositions were prepared by adding certain biocides to molten paraffin wax (m.p. 60—62°C) maintained at a temperature of 100°C.

Test plates 14" x 44" were coated with the different film-forming compositions by dipping into the molten wax at 100°C. The films had an average thickness of 150 micrometres. The test plates were immersed in the sea at a heavy fouling site at Singapore for a six week period. The average sea temperature during the immersion period was 29°C. The degree of fouling on the surface was then assessed and rated on a scale ranging from 1—10. On a plate rated 10, heavy fouling occurred; organisms including barnacles, filamentous algae, hydroids and ascidians were all present. On a plate rated 1, only microbial fouling was present and this did not cover more than 50 per cent of the surface.

The results are shown in Table 1 below.

TABLE 1

	Biocide	Parts by weight paraffin wax	Parts by weight of biocide	Thermal stability of biocide	Solubility of biocide in wax	Solubility of biocide in water when incorporated in wax coating	Fouling Rating 1-10
1	Control	100	0	—	—	—	10
2	copper naphthenate	80	20	stable at 150°C	Excellent	Insoluble	3
3	Zinc stearate	80	20	stable at 150°C	Excellent	Insoluble	2
4	4-chloro-m-cresol	80	20	Fumes evolved at 150°C	Excellent	Insoluble	3
5	Givgard DXN	80	20	Boils 66-68°C at 3mm Hg	Soluble	Insoluble	2
6	Chloramine T	90	10	Moderately thermally stable	Slightly Soluble	Reacts slowly with water	5
7	p-dichlorobenzene	80	20	stable at 150°C	Soluble	Insoluble	5
8	Monuron	95	5	mpt 158-159°C	Slightly Soluble	Insoluble	5
9	Poly (zinc methacrylate	71.5	28.5	stable at 150°C	Insoluble but Dispersible	Slightly Soluble	1
10	Polyionene-2,4-chloride	80	20	Stable at 150°C	Slightly Soluble	Insoluble	1
11	Polyionene-2,6-bromide	83	17	Stable at 150°C	Dispersible	Insoluble	3
12	Poly (nickel acrylate)	67	33	Stable at 150°C	Dispersible	Insoluble	5

(16)

The following examples describe the preparation of the compounds used in Examples 9 to 12.

Example 13.

Preparation of poly (zinc methacrylate) of Example 9.

5 40 g of a polymethacrylic acid water solution (20% polyacid) was further
diluted with 150 mls H₂O and heated to approximately 50°C. To the stirred
(Silverson stirrer) solution was added dropwise 25 mls 2M NaOH solution. 25 mls
of 1M Zinc sulphate solution was then added dropwise to the stirred solution with
the formation of a white precipitate. 10 g of the poly(zinc methacrylate) material
was isolated. 10

Example 14.

Preparation of polyionene chloride of Example 10.

15 12.5 (0.1 mole) di-chloro-butene-2 was added dropwise to a stirred solution of
11.6 g (0.1 mole) of N,N,N',N'-tetramethylethylene diamine in 25 mls of water.
The reaction mixture was stirred for 120 hours at 20°C and consequently poured
into a large excess of vigorously stirred acetone. The precipitated ionene was
filtered off and dried in vacuum at 60°C (yield 23 g). The viscosity of the polymer
in 0.4 M KBr. was 0.0109 m³/kg. 15

Example 15.

Preparation of polyionene bromide of Example 11.

20 12.2 g (0.05 moles) of 1,6-dibromohexane was added dropwise to a stirred
solution of 5.8 g (0.05 moles) of N,N,N',N'-tetramethylethylene diamine in 12.5
mls of dimethylformamide/H₂O (4:1 vol.) solvent mixture. The reaction mixture
was stirred for 24 hrs. at 20°C, and consequently poured into a large excess of
vigorously stirred acetone. The precipitated ionene was filtered off and dried in
vacuum at 60°C (yield 13 g). The viscosity of the polymer in 0.4 M KBr was
0.0121 m³/kg. 25

Example 16.

Preparation of poly (nickel acrylate) of Example 12.

30 Example 13 was repeated using polyacrylic acid instead of polymethacrylic
acid, and nickel nitrate instead of zinc sulphate. 30

WHAT WE CLAIM IS:—

35 1. A process for coating a surface capable of underwater use with wax,
characterised in that the wax coating has a thickness of from 5 to 500 micrometres
and contains at least one biocide dispersed or dissolved in the wax which is
effective against marine weed and/or shell growth when so dispersed or dissolved. 35

2. A process as claimed in claim 1, wherein the biocide is water-insoluble.

3. A process as claimed in claim 2, wherein the biocide is fresh water-insoluble.

40 4. A process as claimed in claim 1, 2 or 3 wherein the wax coating has a
thickness of from 50 to 300 micrometres. 40

5. A process as claimed in claim 1, 2 or 3 wherein the wax coating has a
thickness of from 10 to 49 micrometres.

45 6. A process as claimed in any of claims 1 to 5 wherein the biocide is soluble in
molten wax. 45

7. A process as claimed in any of claims 1 to 6 wherein the biocide is thermally
stable up to 150°C.

8. A process as claimed in any of claims 1 to 7 wherein the biocide is a metal
salt.

50 9. A process as claimed in claim 8 wherein the metal cation is copper, zinc,
nickel, cobalt, manganese or tin. 50

10. A process as claimed in claim 8 or 9 wherein the anion of the salt is derived
from an organic acid.

55 11. A process as claimed in claim 10, wherein the acid is an alkyl, alkenyl or
aryl carboxylic acid having from 2 to 100 carbon atoms. 55

12. A process as claimed in claim 10, wherein the acid is a polymeric acid
having an average molecular weight of from 200 to 500,000.

13. A process as claimed in claim 12 wherein the acid is polyacrylic acid.

60 14. A process as claimed in any of claims 1 to 7 wherein the biocide is an
organic compound having a biocidally active molecular structure containing S,
Cl, N or O. 60

The following examples describe the preparation of the compounds used in Examples 9 to 12.

Example 13.

Preparation of poly (zinc methacrylate) of Example 9.

5 40 g of a polymethacrylic acid water solution (20% polyacid) was further diluted with 150 mls H₂O and heated to approximately 50°C. To the stirred (Silverson stirrer) solution was added dropwise 25 mls 2M NaOH solution. 25 mls of 1M Zinc sulphate solution was then added dropwise to the stirred solution with the formation of a white precipitate. 10 g of the poly(zinc methacrylate) material was isolated. 10

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15 12.5 (0.1 mole) di-chloro-butene-2 was added dropwise to a stirred solution of 11.6 g (0.1 mole) of N,N,N',N'-tetramethylethylene diamine in 25 mls of water. The reaction mixture was stirred for 120 hours at 20°C and consequently poured into a large excess of vigorously stirred acetone. The precipitated ionene was filtered off and dried in vacuum at 60°C (yield 23 g). The viscosity of the polymer in 0.4 MKBr. was 0.0109 m³/kg. 15

Example 15.

Preparation of polyionene bromide of Example 11.

20 12.2 g (0.05 moles) of 1,6-dibromohexane was added dropwise to a stirred solution of 5.8 g (0.05 moles) of N,N,N',N'-tetramethylethylene diamine in 12.5 mls of dimethylformamide/H₂O (4:1 vol.) solvent mixture. The reaction mixture was stirred for 24 hrs. at 20°C, and consequently poured into a large excess of vigorously stirred acetone. The precipitated ionene was filtered off and dried in vacuum at 60°C (yield 13 g). The viscosity of the polymer in 0.4 M KBr was 0.0121 m³/kg. 25

Example 16.

Preparation of poly (nickel acrylate) of Example 12.

30 Example 13 was repeated using polyacrylic acid instead of polymethacrylic acid, and nickel nitrate instead of zinc sulphate. 30

WHAT WE CLAIM IS:—

35 1. A process for coating a surface capable of underwater use with wax, characterised in that the wax coating has a thickness of from 5 to 500 micrometres and contains at least one biocide dispersed or dissolved in the wax which is effective against marine weed and/or shell growth when so dispersed or dissolved. 35

2. A process as claimed in claim 1, wherein the biocide is water-insoluble.

3. A process as claimed in claim 2, wherein the biocide is fresh water-insoluble.

40 4. A process as claimed in claim 1, 2 or 3 wherein the wax coating has a thickness of from 50 to 300 micrometres. 40

5. A process as claimed in claim 1, 2 or 3 wherein the wax coating has a thickness of from 10 to 49 micrometres.

45 6. A process as claimed in any of claims 1 to 5 wherein the biocide is soluble in molten wax. 45

7. A process as claimed in any of claims 1 to 6 wherein the biocide is thermally stable up to 150°C.

8. A process as claimed in any of claims 1 to 7 wherein the biocide is a metal salt.

50 9. A process as claimed in claim 8 wherein the metal cation is copper, zinc, nickel, cobalt, manganese or tin. 50

10. A process as claimed in claim 8 or 9 wherein the anion of the salt is derived from an organic acid.

55 11. A process as claimed in claim 10, wherein the acid is an alkyl, alkenyl or aryl carboxylic acid having from 2 to 100 carbon atoms. 55

12. A process as claimed in claim 10, wherein the acid is a polymeric acid having an average molecular weight of from 200 to 500,000.

13. A process as claimed in claim 12 wherein the acid is polyacrylic acid.

60 14. A process as claimed in any of claims 1 to 7 wherein the biocide is an organic compound having a biocidally active molecular structure containing S, Cl, N or O. 60



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15. A process as claimed in claim 14 wherein the biocide is a polyionene.
16. A process as claimed in any of claims 1 to 15, wherein the wax contains from 1 to 70% wt. of biocide by weight of wax.
17. A process as claimed in claim 16, wherein the wax contains from 1 to 40% wt. of biocide by weight of wax.
18. A process as claimed in any of claims 1 to 17 wherein the wax has a melting point of from 45 to 120°C penetration of from 1 to 60 mm x 10 by the method of ASTM D1321.
19. A surface capable of underwater use having a wax coating with a thickness of from 5 to 500 micrometres and containing at least one biocide dispersed or dissolved in the wax which is effective against marine weed and/or shell growth when so dispersed or dissolved.
20. A surface as claimed in claim 19, wherein the wax has the characteristics of claim 4, 5, 16, 17 or 18.
21. A surface as claimed in claim 19 or 20 wherein the biocide has the characteristics of claim 2, 3, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15.
22. A process as claimed in claim 1 substantially as described in the Examples.
23. A surface as claimed in claim 19 substantially as described in the Examples.

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