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(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

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problem of choosing short but frequent, or infrequent but long, periods while his ship is out of commission.

To avoid the problem set out above, it has been proposed to coat ships' hulls with a film of wax. Thus UK 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. UK 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 coatings 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 a method of applying the wax that gives a smooth surface without subsequent treatment and which facilitates the incorporation of biocides into the wax.

According to the present invention a process for coating a surface intended for underwater use with wax, comprises applying to the surface an aqueous dispersion of a wax.

The use of an aqueous dispersion of a wax has the following advantages over hot spraying:

1. The wax can be applied more evenly giving a smooth and, in some cases a glossy, film which may not require buffing or polishing.

2. The thickness of the film can be readily controlled by the viscosity of the dispersion and its water content.

3. The wax can be applied at atmospheric temperature using conventional spraying equipment.

4. Biocidal additives can be easily incorporated, if required. Since the wax is applied cold, there will be less toxic hazard from biocidal vapours and no risk of thermal decomposition of the biocide.

The aqueous wax dispersion may be prepared by emulsifying wax and water at a tem-

perature above the melting point of the wax in the presence of an emulsifying agent, and allowing the emulsion to cool.

The dispersion may contain from 15 to 75% wt of wax by weight of the dispersion, preferably from 25 to 60% wt. It may have a viscosity of from 1.5°E to 75° Engler at 20° C, preferably from 2°E to 50°E. The thickness of the final coating will depend on the viscosity, which controls the flow of the dispersion over the surface, and on the water content, since the thickness will reduce as the water evaporates in proportion to the water content.

By suitable control as above, the final coating may have a thickness of from 5 to 500 micrometres, preferably 50 to 300 micrometres.

The wax coating may be applied to surfaces which have not been painted with anti-fouling paint, but is preferably applied on top of an anti-fouling paint, since the paint will afford protection if areas of the wax coating are accidentally damaged or removed. Wax coatings applied by spraying molten wax are substantially impervious to water at any thickness above 5 micrometres and substantially impervious to biocides at thicknesses above 50 micrometres. Wax coatings applied as aqueous dispersions may, however, be more porous and allow a slow controlled migration of toxins through the wax coating from an underlying anti-fouling paint. This migration may be appreciable through coatings of 10—49 micrometres thickness and coatings of such relative thinness can be applied using aqueous wax dispersions. However coatings of 50—300 micrometres may still show controlled migration, providing another potential advantage over films applied by other techniques.

A wide range of waxes may be used, but the wax preferably has a melting point of from 45 to 120° C. and a penetration of from 1 to 60 mm x 10, as measured by ASTM D1321. 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, although, as explained hereafter, the method of forming the dispersions may differ. Blends of two or more types of wax can often be chosen to optimize physical properties, particularly gloss.

The emulsifying agent used to form the dispersion may be present in an amount of from 0.2 to 10% wt by weight of the dispersion, preferably from 1.0 to 5.0% wt. The agent used and the amount used is a factor in ensuring that the dispersion is stable and capable of being stored, in controlling the viscosity, in minimising surface tackiness of the finished coating and in minimising the re-dispersion and stripping of the finished coating by sea-water. Preferably, to minimise stripping, the amount

of emulsifying agent is kept to a minimum, consistent with providing adequate stability and viscosity.

The emulsifying agent may be anionic, cationic, or non-ionic, but preferably the former, because anionic agents best meet the desiderata set out above. Cationic agents are also useful and non-ionic agents are the least preferred.

Examples of suitable agents may be.

Anionic—Amine salts of carboxylic acids, particularly ammoniacal alkylamine, and alkanolamine salts of carboxylic acids having from 4 to 54 carbon atoms, e.g. ammoniacal or ethanolamine salts of stearic or oleic acids.

Cationic—alkylamine hydrohalides, particularly those with alkyl groups having from 4 to 24 carbon atoms, e.g. laurylamine hydrochloride and cetyl trimethyl ammonium bromide.

Non-ionic—sorbitan and sorbitol esters (including oleates) with or without polyoxyethylene groups e.g. the agents sold under the Registered Trade Marks "Span" and "Tween".

Oxidised mineral wax and certain other waxes already contain carboxyl groups so it is only necessary to add a base to form an anionic emulsifying agent. Suitable bases may be as set out above, e.g. ammonia, triethanolamine or morpholine.

The dispersions may be produced by the hot emulsification of molten wax or wax blend and water in the presence of an emulsifying agent. The water may be added to the wax or vice-versa, but preferably water is added to wax so that a water in wax emulsion is first formed, which later inverts to a wax in water emulsion. With anionic agents, the agent is preferably formed in situ, with the base being present in the water phase and the acid in the wax phase. In a further preferment all the base may be added during the first part of the emulsion forming process e.g. the base may

all be present in the first 20% of water added to the wax, pure water being added thereafter. The molar ratio of base to acid may be from 1.0 to 3.0.

The emulsion may be formed in any suitable equipment e.g. a Silverson mixer fitted with an emulsifying head.

For good stability and adequate viscosity, the emulsion preferably is a wax in water emulsion with an average wax particle size of from 0.05 to 10 micrometres.

If required biocides may be incorporated during the formation of the emulsion or subsequently. Wax coatings containing biocides are described and claimed in the complete specification of cognate UK Patent Applications Nos. 11186/74, 11187/74 and 25084/74, Serial No. 1,479,702, and the present invention may be used in combination with this other invention.

The dispersions may be applied by brushing or spraying at atmospheric temperature. Conventional paint spraying equipment may be used.

The present invention includes surfaces intended for underwater use having a wax coating applied as previously described. 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.

Example 1.

Effect of Emulsifier Concentration.

The following experimental conditions were used.

Wax: Paraffin wax of 60/62° C. melting point.

Mode of Addition: Water to wax

Temperature of addition: 80°

Rate of cooling: Rapid, in ice

Emulsifier: Triethanolamine stearate formed in situ from triethanolamine dissolved in the wax and stearic acid in the wax.

Parts by wt. wax	Parts by wt. Emulsifier	Parts by wt. Water	Comments
35	1.5	63.5	Poor emulsification
35	2.5	62.5	Fairly stable. After 17 days 10% separation. Re-disperses on shaking.
35	3.0	62	After 17 days. 8% separation. Re-disperses on shaking.
35	3.5	61.5	After 17 days. 2% separation. Emulsion thick, disperses on stirring.

Modifying the mode of addition so that all the triethanolamine was added with the first 20% of the water i.e. so that the triethanolamine stearate was formed before the bulk of the water was added, enabled emulsifier concentrations as low as 1.5 and 2.0 parts by weight to be used with the following values of wax particle size.

Emulsifier content parts per 100 per weight	Wax Particle Size	Separation After 12 days
1.5	4-8 μ m	22%
2.0	12-18 μ m	26%

10 Example 2. Temperature: 85° C
Effect of Emulsifier type. Cooling: Rapid, in ice
The following experimental conditions were Emulsion formulation:
employed. Parts by wt. of 60/62° C. Paraffin wax—20
Mode of Application: Water to wax Parts by wt. of Emulsifier — 2

Emulsifier	Stability of Dispersion	Viscosity	PROPERTIES OF SPRAYED FILM	
			Cohesive and Adhesive properties	Life in sea water
Ammonium Stearate (anionic)	Very good	thick >50°E	Good	Good
Laurylamine Hydrochloride (cationic)	Moderate but easily re-dispersed	very thin 3°E	Good	Good
Span 80 Tween 80 mixture with + *HLB = 10 (non-ionic)	Very small separation overnight	thin 10°E	Sprayed film has a long drying time (48 hrs.) and is relatively soft	Moderate

* hydrophile — lypophile balance

The films were produced by spraying the dispersions onto steel plates using a DeVilbiss paint spray gun at an air pressure of 35 psig.

It will be seen that both anionic and cationic emulsifiers gave good wax films and that the anionic emulsifier gave a stable dispersion. The cationic dispersion was a less stable thinner dispersion but it could be readily redispersed. The non-ionic emulsifier gave a stable dispersion but only moderate film properties.

Example 3.

Anti-fouling properties of wax films.

Dispersions prepared from paraffin wax and ammonium stearate as in Example 2 were sprayed onto two steel plates, one painted with "Latenac" anti-fouling paint and one painted with an ordinary anti-corrosion paint. The wax films on each plate were 80—120 micrometres thick.

The plates were immersed in sea water at Singapore for 6 weeks and then examined. The plate of wax on top of ordinary paint was fouled by barnacles and hydroids; the plate of wax on top of anti-fouling paint was free of any growth. The wax coating produced from an aqueous dispersion was thus sufficiently porous to allow the controlled leaching of toxins from the underlying anti-fouling paint.

Example 4.

Effect of viscosity on coating thickness.

Dispersions were formed as in Example 2, but using different amounts of emulsifier to give dispersions of differing viscosity. The dispersions were sprayed onto steel plates as in Example 2. The table below shows how the thickness of the film can be varied by varying the viscosity.

Emulsifier: triethanolamine stearate

Parts by wt. Paraffin wax	Parts by wt. Emulsifier	Viscosity	Thickness of Sprayed film
25	5	20°E	150 μ
35	1.5	5°E	80 μ
35	2.5	15°E	120
35	3.5	50°E	200 μ

All the films had smooth surfaces, the surface roughness being less than 3 centre line average.

WHAT WE CLAIM IS:—

1. A process for coating a surface intended for underwater use with wax, characterised in that the wax is applied as an aqueous dispersion of a wax

2. A process as claimed in claim 1 wherein the dispersion contains from 15 to 75% wt, preferably 25 to 60% wt, of wax by weight of the dispersion.

3. A process as claimed in claim 1 or 2 wherein the dispersion has a viscosity of from 1.5 to 75° Engler at 20° C., preferably from 2°E to 50°E.

4. A process as claimed in claim 1, 2 or 3 wherein the finished wax coating has a thickness of from 5 to 500 micrometres.

5. A process as claimed in claim 4 wherein the finished wax coating has a thickness of from 50 to 300 micrometres.

6. A process as claimed in claim 4 wherein the finished wax coating has a thickness of from 10 to 49 micrometres.

7. A process as claimed in any of claims 1 to 6 wherein the wax has a melting point of from 45 to 120° C. and a penetration of from 1 to 60 mm $\times$ 10 as measured by ASTM D1321.

8. A process as claimed in claim 7 wherein the wax is a mineral wax.

9. A process as claimed in any of claims 1 to 8 wherein the dispersion is formed by emulsifying water and wax at a temperature above the melting point of the wax in the presence of an emulsifying agent and cooling the emulsion.

10. A process as claimed in claim 9 wherein the amount of emulsifying agent is from 0.2 to 10% wt, preferably from 1.0 to 5.0% wt, by weight of the dispersion.

11. A process as claimed in claim 9 or 10 wherein the emulsifying agent is anionic.

12. A process as claimed in claim 9, 10 or 11 wherein water is added to wax to form the emulsion.

13. A process as claimed in claim 11 or 12 wherein the acid portion of the anionic emulsifying agent is in the wax and the base portion in the water.



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The films were produced by spraying the dispersions onto steel plates using a DeVilbiss paint spray gun at an air pressure of 35 psig.

It will be seen that both anionic and cationic emulsifiers gave good wax films and that the anionic emulsifier gave a stable dispersion. The cationic dispersion was a less stable thinner dispersion but it could be readily redispersed. The non-ionic emulsifier gave a stable dispersion but only moderate film properties.

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4. A process as claimed in claim 1, 2 or 3 wherein the finished wax coating has a thickness of from 5 to 500 micrometres.

5. A process as claimed in claim 4 wherein the finished wax coating has a thickness of from 50 to 300 micrometres.

6. A process as claimed in claim 4 wherein the finished wax coating has a thickness of from 10 to 49 micrometres.

7. A process as claimed in any of claims 1 to 6 wherein the wax has a melting point of from 45 to 120° C. and a penetration of from 1 to 60 mm $\times$ 10 as measured by ASTM D1321.

8. A process as claimed in claim 7 wherein the wax is a mineral wax.

9. A process as claimed in any of claims 1 to 8 wherein the dispersion is formed by emulsifying water and wax at a temperature above the melting point of the wax in the presence of an emulsifying agent and cooling the emulsion.

10. A process as claimed in claim 9 wherein the amount of emulsifying agent is from 0.2 to 10% wt, preferably from 1.0 to 5.0% wt, by weight of the dispersion.

11. A process as claimed in claim 9 or 10 wherein the emulsifying agent is anionic.

12. A process as claimed in claim 9, 10 or 11 wherein water is added to wax to form the emulsion.

13. A process as claimed in claim 11 or 12 wherein the acid portion of the anionic emulsifying agent is in the wax and the base portion in the water.



14. A process as claimed in claim 13 wherein all of the base portion is present in the first 20% of the water added.

5 15. A process as claimed in any of claims 9 to 14 wherein the emulsion is a wax in water emulsion having an average wax particle size of from 0.05 to 10 micrometres.

16. A process for coating surfaces intended

for underwater use with wax as described in the Examples.

17. Surfaces, intended for underwater use, whenever coated with wax by a process as described in any of claims 1 to 16.

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