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Method and substance for protection of free metallic surfaces, especially steel surfaces against corrosion.

5 The invention relates to a method for protection of free metallic surfaces, especially steel surfaces, against corrosion, whereby the surface is kept in a wet condition.

10 Surfaces which are constantly immersed in water can be given a very effective protection against corrosion by simple and relatively cheap means. With the use of cathodic protection in the form of sacrificial anodes or in the form of impressed current large steel structures can be kept free from corrosion. For this reason drilling platforms or production platforms are normally not painted on

15 the areas which are submerged in water.

 Ships with effective cathodic protection can be completely free from corrosion even on large areas of the flat bottom where the paint has been removed after touching bottom. These examples show how effective cathodic protection can be under water, and also buried pipe lines and tanks both offshore and onshore can be protected by the use of cathodic protection, even though in this

20 case normally combined with coatings of different types.

 Tanks, containers and pipe lines with circulating water for instance can be protected inside by the addition of inhibitors, either inorganic or organic, under inhibitors also understood substances which remove oxygen from the water such as sodium sulfite and hydrazine. Corrosion protection can also be obtained by making the water alkaline.

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 On surfaces in open air, particularly in marine and industrial environments, other normally more expensive methods must be used. On steel galvanizing or painting, or eventually a combination of the two, is the most usual. In these cases the steel must normally be either pickled or sandblasted prior to the application of the corrosion preventing coating.

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 The corrosion problems are particularly big on

surfaces which in marine or industrial environments are alternately dry and wet. Such examples are the splash zones on structures in the sea and pipe tunnel and the like which are particularly exposed to condensation. On
5 such surfaces paints for example perform very poorly.

The present invention aims at solving the practical and not the less the economical problems connected with the protection of steel surfaces and other metallic surfaces, when the said surfaces are not submerged more or
10 less constantly in water, by ensuring that the surfaces either the whole time or at least a considerable part of the time, are covered with a layer of water of sufficient thickness.

The solution of the present invention is to provide a method
15 and a substance as described in the claims.

The term "free metallic surfaces" is meant to include uncovered surfaces and other surfaces which are laying open to the environment, i.e. not embedded in another material.

20 The method of the present invention consists in the binding of a water layer of sufficient thickness to the surface with the help of hydrophilic polymers and/or already known inorganic gel-forming substances, such as metal salt gelling agents, either by increasing the
25 viscosity of the water to such an extent that it does not run off the surface or by cross-linking, understood in the widest significance of the word. Examples are known of cross-linked hydrophilic polymers for instance which can bind up to 49 times their own weight of water.

30 The methods has the very special peculiarity that it is actually an advantage for certain applications if the surface is already corroded as the corrosion products will participate to make it possible to bind a thicker water layer on the surface than on a smooth non-corroded
35 surface. Water-soluble corrosion products can also be utilized in the method by participating in the cross-linking of the hydrophilic polymers.

For applications where the surface the whole time or

a great part of the time is under water containing salts, the method will have the effect of an enrichment of ions in the gel compared with the salt-containing water outside the gel. This higher concentration of ions affords an added conductivity for direct current and consequently a better distribution of the cathodic protection. This is particularly important for areas of the structure with a complicated configuration where it can be difficult to accomodate the anodes properly, but the gel generally affords a lower current density demand for the same degree of cathodic protection.

For applications where periods of high humidity alternate with dry periods, the gel-like layer of water can be cross-linked particularly strognly on the surface so that the evaporation is as low as possible.

A gel-like water layer in accordance with the method will in itself reduce the rate of corrosion by reducing the diffusion of oxygen to the surface. Further corrosion protection can be obtained by combining the method with one or more of the already known methods for the protection of surfaces which are constantly immersed in water, i.e. cathodic protection, addition of corrosion inhibitors, regulation of pH etc.

On surfaces which are parts of a larger surface of which some is immersed in water and on the immersed part equipped with cathodic protection, the effect of the cathodic protection will be extended to at least a part of the surface which has been treated in accordance with the method. This will for one thing be the case of the difficult spalsh zone.

Ballast tanks for instance in ships is another example of applications where cathodic protections can be extended to areas which are not immersed in water with the help of anodes below water.

A surface to be protected by the method of the invention can first be coated with a metal which is anodic relative to the surface, such as zinc powder, and thereafter be coated with hydrophilic polymers and water to

form a gel. The applied metal particles will act as anodes and afford cathodic protection to the surface.

The hydrophilic gel-forming substances can be applied in two stages, on steel as an example first a cationic polymer and thereafter an anionic gel-former. As example of such a combination can be mentioned polyethylenimine, a cationic polymer, and calcium lignin sulfonate cross-linked with a dichromate as anionic gel-former. On certain metals such as aluminium and zinc the opposite sequence can be advantageous.

Many surfaces are besides being exposed to corrosion also exposed to mechanical wear and tear. This is the case for one thing for the underside of vehicles such as cars. Such areas can consequently be in need of protection also against the mechanical stresses. This can then be obtained either by preformed types of coatings, such as plastic covers under the mudguard on cars, or by reinforcing the gel-like water layer in situ on the surface, e.g. with the use of polyurethane foam and similar.

Among hydrophilic polymers well suited for the method can be mentioned such natural polymers as arabic, tragacanth and karaya gums, semi-synthetic such as carboxymethyl cellulose, methylcellulose and other cellulose ethers, lignin derivatives, as well as different types of modified starches (ethers and acetates) and synthetic such as polyacrylic acids, polyacrylamides, polyethylene oxide, polyvinyl pyrrolidone, polyethylenimine and others, as well as combinations of these between themselves or with other substances. There exists a large number of hydrophilic polymers which can be used with the method and the above enumeration is not to be considered as complete.

The particular conditions of technical, practical and economical character of the different areas of application will be decisive for which types of hydrophilic polymers will be preferred. The characteristic common denominator is the property to bind a sufficient quantity of water in the form of a gel to the surface so that it is covered by a continuous water film.

The application of the hydrophilic polymers can be made by using already known methods and the gel formed by water already present on the surface or by water applied to the surface afterwards. In the form of powders the hydrophilic polymers can for instance be applied by electrostatic spray equipment for powder, as a dispersion or a solution the application can be made with airless spray equipment, to have mentioned examples of suitable methods of application.

Hydrophilic polymers can be cross-linked either by using a combination of one strongly anionic and one strongly cationic type or by the use of known cross-linking agents of which can be mentioned poly-functional water-soluble metals and di- or multifunctional organic substances. The most usual cross-linking agents are mentioned in the literature on the different types of hydrophilic polymers. The degree of cross-linking can be adjusted so as to obtain the best combination of mechanical properties and water-binding properties.

The hydrophilic polymers can eventually be combined with for instance fibrous fillers which can impart to the gel-like water layer greater mechanical strength, or porous fillers such as Aerosil^(Registered Trade Mark) which for one thing can add to the binding of water to the surface, or with other substances which give technical or economical advantages.

As examples of inorganic gel-forming substances, which can either be used alone to form a gel-like water layer on the surface or in combination with hydrophilic polymers, can be mentioned silicic acid, aluminium hydroxide, bentonite.

The gel-forming hydrophilic polymers can be applied as monomers, dimers, trimers or prepolymers, which are polymerized/cross-linked during the blending- and application process and in situ. Examples of this are polyacrylamide applied as acrylamide, polyacrylate as acrylate, aminoplast and ureaplast as urea/formaldehyde, resorcinol/formaldehyde, tannin/formaldehyde etc.

Besides pure inorganic gels of for instance

silicates, alumina, magnesia, magnesia/bentonite etc. are also known combined organic/inorganic gels which are well suited for the method.

5 An extensive patent and other literature is known treating gels for the stabilization of soils and for oil drilling.

The major part of these gels could be used with the method of the present invention.

10 The invention is not limited to the method for protecting the metallic surfaces, but does also include the substance used for protecting and a ship protected according to the method.

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CLAIMS:

1. A method for coating a free metallic surface for protecting against corrosion, comprising keeping the surface in a wet condition by binding a water layer to the surface by means of a gel-forming hydrophilic material, which after gelling is essentially insoluble in water.
2. A method according to claim 1 wherein a polymer and/or an inorganic gel-forming substance is (are) used as the hydrophilic material.
3. A method according to claim 2 wherein the hydrophilic polymers and/or inorganic gel-forming substances are cross-linked.
4. A method according to claim 1 wherein the hydrophilic polymers and/or inorganic gel-forming substances are applied to the surface in the form of powders, in the form of a dispersion or in the form of a solution.
5. A method according to claim 1 wherein the gel-formed water containing layer contains corrosion inhibitors.
6. A method according to claim 1 wherein one or more lignin derivatives are used as hydrophilic polymers.
7. A method according to claim 1 wherein two different hydrophilic polymers are used in a non-stoichiometric ratio.
8. A method according to claim 1 comprising first coating with a cationic substance, for instance a cationic polymer, and thereafter an anionic gel-forming substance, or first coating with an anionic substance, for instance



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an anionic polymer, and thereafter a cationic gel-forming substance.

9. A composition for use in protecting free metallic surfaces against corrosion comprising a gel-forming hydrophilic material, which is essentially insoluble in water, preferably a polymer, and/or an inorganic gel-forming substance, together with water and which, on application to the free metallic surface binds the water to the surface.

10. A ship in which one or more the ship's ballast tanks are treated in accordance with the method, described in one of the claims 1-8.

11. A method for the protection of free metallic surfaces against corrosion comprising binding to a metallic surface to be protected a water layer by means of a gel-forming hydrophilic material.

12. A method for the protection of free metallic surfaces substantially as hereinbefore described.
