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## ANTICORROSION AGENT

Rudolf Kern, Oschatz, Germany, assignor to firm:  
Chemische Fabrik R. Baumheier Kommanditge-  
sellschaft, Oschatz-Zschollau, Germany

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This invention relates to agents for preventing or retarding corrosion of various materials such as metals and metal alloys, stones, cement, concrete and wood. The anti-corrosion agents of this invention are also useful in the protection of coatings applied to articles composed of materials such as those mentioned just above. The invention contemplates anti-corrosion agents of a type which protects against the action of gases, such as air, oxygen, and the like, and of liquids and their vapors, such as water, benzine, and the like, as well as of liquids of the type just mentioned in combination with other liquids serving as solvents.

Still more specifically, the invention has in view the employment of the improved protecting agents in the form of paints or coatings. Such coatings are especially useful when employed for the purpose of counteracting corrosion of metals and metal alloys, particularly steels and iron-containing metals. When these metals are exposed for long periods of time, considerable losses are incurred as a result of the corrosive action of air and water, as a result of rusting. It is to be understood, however, that the present invention is not limited in its application to steels and iron-containing metals, since the invention is also of advantage in affording protection against corrosion of other materials.

Heretofore it has been proposed to eliminate corrosion by shielding or protecting materials from air and humidity or other corrosive agents by means of coating the surfaces of such materials with a compound containing a base or binding agent such, for example, as asphalt, tar, coal-tar pitch, resin, artificial resin, lacquers, varnishes, rubber, and the like. These coating materials, however, are subject to cracking after some time of use, and as a result considerable corrosion then takes place at the base of the cracks. Although the cracks may initially be as fine as hair lines, the corrosion undermines and loosens the remaining coating and exposes more and more surface of the material intended to be protected. In this connection it has been proposed to employ the base or binding agent or the coating itself as a solvent for substances adapted to counteract corrosion of the areas of the surface exposed, for example, a metal surface, when cracking develops.

Substances of this kind must necessarily be of different types, as no one of them is suitable for all metals. In carrying out another prior practice, in many cases protection is effected by rendering the surface inactive or passive by pro-

ducing and maintaining on it a protective layer or film, for example a film of oxide or of sulphide.

Still another practice sometimes followed is based on the fact that corrosion is frequently initiated by fungi, algaceous plants, pseudolichen; microbes or other micro-organisms. Plants or organisms of this type may settle upon the surface of a material to be protected, or may come in contact with the surface in coatings or films applied thereto or formed thereon spontaneously. Protection in accordance with this method involves destroying the accumulation or growth of the plants or organisms and this, of course, removes an agent tending to initiate corrosion. This practice has been especially intended for use with paints for vessels or submerged construction work.

It has also been found that for protecting the several metals from corrosion, the following substances may be employed to advantage: for iron and its alloys, such as steel, the protective substances should be of that type which are capable of imparting to water an alkaline reaction, for instance alkalis themselves, alkali carbonates, ammonium, and amines of organic origin. In an alkaline medium, iron behaves more like a precious metal than when immersed into an acid solution. In an alkaline medium the iron appears to be rendered passive. Aluminum, cadmium, and zinc are best protected by a film of oxide; silver by a film of oxide, or sulphide, or chloride; and lead preferably by a layer of carbonate.

It has been recognized, particularly in paints intended for use on vessels, that it is useful to add to the coating some compound or compounds which, because of their high biological effect, prevent the action or growth of micro-organisms either of animal or of vegetable origin.

In accordance with prior practice, the compounds mentioned are dissolved either in coatings or in paints so as to serve as anti-corrosion media, although this has been attended with but little success. In the first place, solutions of this type are open to the objection that the properties of the binding or coating medium are unfavorably altered by the substance dissolved therein as, for instance, by changing the physical properties thereof, or by softening or hardening the coating, or making it more brittle, or by changing its chemical behavior. In this way various characteristics of the coating are unfavorably influenced, such as its age, resinification, and formation of film, sometimes even causing porosity, or causing, by alkaline additions, saponification

of the resins and swelling up of the soaps produced. This also tends to promote a more or less hygroscopic character, thus allowing water to pass through and accelerate corrosion, instead of preventing it. In the second place, it has been found that, for good protection, considerable quantities of anti-corrosion media are required, although in most instances the dissolving power of the coating or binding medium is relatively limited.

The present invention is concerned with overcoming, to a considerable degree, objections of the type mentioned above. In accordance with this invention, the protective agents are employed in the form which will make it possible to use binding agents or coating media of the types which will not (or only to a slight extent) dissolve the protective substance. The result of this is that, in spite of high concentrations of the protective agents, an unfavorable influence of the protective substance upon the binding agent or coating medium is completely avoided.

In accordance with the present invention, instead of dissolving the protective media in the coating or binding medium itself, the protective media are dissolved in a substrate. The protective media employed when practicing this invention are gases, vapors or substances of readily gasifying, evaporating or volatile character. The substrate employed may desirably be absolutely insoluble in the coating or binding medium and thus carried in suspension. Pigments having coloring properties may be used as the substrate, or the substrate may take the form of a mere addition to the coating medium. The power of the substrate for dissolving or adsorbing the protective substance must, of course, be high. With this in mind, the invention contemplates use of substances which are porous or have large surface area.

Substances of the type mentioned are capable of adsorbing gases and vapors, and often free large amounts of heat during adsorption. The dissolving process, therefore, is exothermic, whereas elimination of the dissolved or adsorbed substance out of the substrate constitutes an endothermic process. Such substrates charged with protective substances thus constitute a reservoir from which the protective agents are liberated, in quantities sufficient for the desired purpose, over a long period of time and at a uniform rate. As examples of porous pigments I may mention the following: carbon, such as charcoal, and other active and activated carbons, coke, silica gels, synthetic silicates like "Permutit", fuller's earth, and kieselguhr. Oxides are also suitable, such for instance as precipitated alumina, oxides of iron, and oxide of titanium, slags, such as slags of lignite, and zinc oxide. In addition, porous materials of the following types may be used: amorphous or microcrystalline sulphides, like lead sulphide or cadmium sulphide, amorphous phosphates or silicates, like those of aluminum, and the oxides of lead, like litharge and minium.

The foregoing adsorbents are used with protective substances of the following types, which are grouped for the sake of clarity:

(1) Substances which show an alkaline reaction in the presence of water or in the presence of compounds of hydroxide having organic origin. The following are mentioned as examples of these: ammonia, amines like methylamine, propylamine, ethyldiamine, piperidine, pyridine, benzylamine, methyl aniline, and ethanolamine;

(2) Substances of organic or inorganic origin having a neutral or slightly acid reaction. For instance: carbonic acid, hydrogen, oxygen, ozone, hydrogen sulphide, ethane, propane, hexane, ethylene, acetylene, diethyl ether, benzene, methylene chloride, chloroform, alkyl esters like alkyl nitrates and alkyl nitrites, fluorides, and sulphides;

(3) Substances of highly toxic character. For example: carbon monoxide, trichloronitromethane, cyanogen halogenite, hydrogen cyanide, bromoacetone, chloracetophenone, readily volatilizable metallo-organic compounds like tetraethyl lead, nickel carbonyl, and other tertiary bases (whose poisonous heavy metallic salts may be precipitated on the large surface area of the porous substrate) like those of mercury, copper, silver, thallium, and lead, organic derivatives of arsenic hydrides and hydrogen phosphides, and halodialkyl sulphides. Nicotine and chinoline are other substances suitable for the purpose of having a toxic effect.

It should be noted in connection with the foregoing groups that frequently certain substances mentioned in one group also have the characteristics of substances mentioned in other groups. For example, among the substances mentioned in groups 1 and 2 there are a number possessing highly toxic characteristics.

In accordance with the invention, one or more of the porous substances suggested may be employed, and it is also possible to charge the substances with more than one volatile or protective agent. Still further, the gases or vapors may be fixed on the substrate, as by treatment with metallic salts.

If desired, the porous substances of this invention having adsorbed protective agents may be used in the paint or coating medium in combination with other agents for resisting corrosion which are dissolved or suspended in the binding medium itself, although such other agents may not necessarily be charged with protective substances in the manner described above. As examples of these additions I mention especially the metals already proposed as anti-corrosion agents (for instance lead, aluminum, copper, zinc, powdered iron and the like). The metalloids (carbon and the like) may be used, as may also other metallic oxides (oxides of lead, oxides of iron, zinc oxide, and the like). Still further, the following substances may be employed: metallic sulphides and compounds thereof such as lithopones, chromates (lead chromate), nitrites and other colored and uncolored inorganic pigments like white lead and chromic oxide.

As coating media and binding agents for the same, the following are mentioned as suitable examples: asphalt, wood tar oil, tar, drying oils, varnishes, lacquers (including those on cellulose ester and ether bases), resins, artificial resins, rubber solutions, gelatine, casein, and emulsion binding agents. These agents may contain either the usual driers like cobalt resinate, lead manganese oleate, manganese resinate, and the like, or the usual neutral diluting substances such as oil of turpentine, lacquer benzene, and the like.

The protective effect attained according to the invention is particularly noticeable when employing neutral varnishes, especially neutral linseed oil varnishes or varnishes having a low acid number.

The anti-corrosion agents of this invention may be used in the protection of building materials like cement, concrete, artificial stones, nat-

ural stones such as sandstone, wood, tile, and materials having similar composition. My improved agents may also be applied to metals such as those mentioned above as well as others, for instance, tin, and alloys, of which might be mentioned "Stellite" (chromium and cobalt), "Monel" metal (nickel and copper), brass (copper and zinc), bronze (copper and tin; aluminum and copper).

As has already been pointed out, the protective medium to be used must be chosen in accordance with the material to be protected and the purpose in view, while bearing in mind also the nature of the coating medium and binding agent to be employed. One skilled in the art may obviously select the protective agent best suited to any particular material and purpose. The present invention indicates the manner in which to proceed in order to apply such protective media in highly concentrated form without producing any undesirable effect upon the coating and binding materials.

The following examples will serve to illustrate the manner of practicing the present invention, although they are not to be considered as limiting the scope of the appended claims.

#### Example 1

460 parts by weight of varnish are mixed with 135 parts by weight of activated carbon in powdered form and containing 6% by weight adsorbed anhydrous ammonia gas. Then 296 parts by weight of minium and 115 parts by weight of lead powder are added. A coating prepared in this way dries well and has a strong protective effect upon iron, steel, nickel, and chromium. Iron, when treated with this mixture, is rendered passive.

#### Example 2

A protective anti-corrosion coating which is excellently suited for protecting iron and also galvanized iron, is one containing 410 parts by weight of varnish, 80 parts by weight of active carbon charged with ether vapor in vacuo to provide 16% adsorbed ether vapor content, 210 parts by weight of minium, and 150 parts by weight of zinc powder.

#### Example 3

For protecting vessels, a paint of the following character may be employed: 400 parts by weight of varnish of linseed oil, 180 parts by weight of minium charged with pyridine vapor and with the base precipitated with bichloride of mercury, 50 parts by weight of cobalt resinate, 60 parts by weight of charcoal charged up to 2% with nitrobenzine vapor, 180 parts by weight of copper powder, and 100 parts by weight of oil of turpentine.

#### Example 4

Another anti-rust paint comprises 800 parts by weight of linseed oil varnish, 250 parts by weight of kieselguhr treated with acetylene up to saturation, 600 parts by weight of minium, 110 parts by weight of lead powder, and 90 parts by weight of pulverized iron. Instead of kieselguhr, silica gel or some silicic acid gel may be used.

#### Example 5

For protecting copper and its alloys a mixture composed of 600 parts by weight of linseed oil varnish, 350 parts by weight of micaceous iron ore, 60 parts by weight of activated carbon charged with hydrogen sulphide, and 80 parts by

weight of manganese resinate has been found to be particularly effective.

#### Example 6

600 parts by weight of coal tar are mixed, by vigorous agitation, with 120 parts by weight of a mixture containing equivalent parts of colloidal alumina and activated carbon, these substrates having been previously charged with carbonic acid. In case this mixture is too thick (as a consequence of the condition of the tar), the characteristics may be improved by adding a neutral diluting medium, for instance petrol or benzine, in a quantity sufficient to obtain the desired suspension. If preferred, carbon may be employed as the sole pigment, and in this event the carbon may be used in a charged condition, i. e., charged with silicic fluoride, or with hydrofluorsilicic acid, or with silanes.

To illustrate the improved action secured when following the present invention, the following test data is given:

Small sheets of steel were covered with a paint prepared in accordance with Example 1 above, the said paint containing neutral varnish, lead in powder form, minium and activated carbon charged with ammonia. These small plates were suspended in the cooling tower of a power generating station in which they were uninterruptedly sprinkled with water of the following characteristics: temperature—30° C., degree of hardness—160 (German standard), 2000 mg. combined chlorine to each liter of water, 565 mg. combined SO<sub>2</sub> per liter of water, from 5000 to 6000 mg. salts per liter of water, 100 mg. combined nitric acid per liter of water, and as much oxygen as the water might be capable of retaining. After a four weeks' treatment period, the sheets did not show any traces of rusting, even after removal of the paint by means of a sodium hydroxide solution. Other paints, including those heretofore recognized as best, were also applied to test samples and tested at the same time. These others were unable to prevent rusting.

I claim:

1. A coating composition for surfaces subject to corrosive influences comprising a fluid vehicle and a corrosion resistance producing ingredient, said ingredient comprising a finely divided and highly porous substrate carrying an adsorbed corrosion inhibitive substance effective to inhibit corrosion at the temperature of use over a prolonged period, said substrate in effect constituting a reservoir for the corrosion inhibitive substance, and said ingredient being substantially insoluble in and substantially inactive with respect to the vehicle and said substrate with its adsorbed inhibitive substance being present in a quantity sufficient to substantially eliminate corrosion throughout a prolonged period.

2. A coating in accordance with claim 1 in which the substrate is chosen from the class consisting of adsorptive forms of carbon and inorganic siliceous materials.

3. A coating in accordance with claim 1 in which the corrosion inhibitive substance is a gas.

4. A coating in accordance with claim 1 in which the corrosion inhibitive substance is volatile at a temperature within the range encountered in use.

5. A coating in accordance with claim 1 in which the corrosion inhibitive substance is volatile and has an alkaline reaction in the presence of water.

6. A coating in accordance with claim 1 in

which the corrosion inhibitive substance is ammonia.

7. A coating in accordance with claim 1 in which the corrosion inhibitive substance has a toxic effect upon lower organisms.

8. A coating in accordance with claim 1 in which the finely divided and highly porous substrate is a pigment.

9. A coating or paint in accordance with claim 1 in which the corrosion inhibitive substance is precipitated on the substrate by treatment with a salt of a metal chosen from the group consisting of mercury, copper, silver, thallium and lead, to produce a salt.

10. A coating in accordance with claim 1 in which the vehicle is resinous.

11. A coating in accordance with claim 1 in which the vehicle comprises a neutral varnish.

12. A coating composition for surfaces subject to corrosive influences comprising a fluid vehicle and a corrosion resistance producing ingredient, said ingredient comprising a finely divided and highly porous substrate carrying a corrosion inhibitive substance adsorbed thereon in gaseous form effective to inhibit corrosion at the temperature of use over a prolonged period, said substrate in effect constituting a reservoir for the corrosion inhibitive substance, and said ingredient being substantially insoluble in and substantially inactive with respect to the vehicle and said substrate with its adsorbed inhibitive substance being present in a quantity sufficient to substantially eliminate corrosion throughout a prolonged period.

RUDOLF KERN.