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(72) Inventors: JOHN MALCOLM SENIOR
NICHOLAS THOMAS CORKE

(19) THE PATENT OFFICE LONDON

(54) HEAT-RECOVERABLE ARTICLE AND METHOD OF PROTECTING METAL SUBSTRATES

(71) We, RAYCHEM LIMITED, a British company of Rolls House, 7 Rolls Buildings, Fetter Lane, London EC4., 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 methods for the protection of substrates from environmental attack and to heat-recoverable articles suitable for use in such methods.

Heat-recoverable articles, especially heat-shrinkable articles, are now widely used in many areas where insulation, sealing and encapsulation are required. Usually these articles recover, on heating, towards an original shape from which they have previously been deformed, but the term "heat-recoverable", as used herein, also includes an article which, on heating, adopts a new configuration, even if it has not been previously deformed.

In their most common form, such articles comprise a heat-shrinkable sleeve made from a polymeric material exhibiting the property of elastic or plastic memory as described, for example, in U.S. Patents 2,027,962, 3,086,242 and 3,597,372. As is made clear in, for example, U.S. Patent 2,027,962, the original dimensionally heat-stable form may be a transient form in a continuous process in which, for example, an extruded tube is expanded, whilst hot, to a dimensionally heat-unstable form but, in other applications, a preformed dimensionally heat stable article is deformed to a dimensionally heat unstable form in a separate stage.

In other articles, as described, for example, in British Patent 1,440,524, an elastomeric member such as an outer tubular member is held in a stretched state by a second member, such as an inner tubular member which, upon, heating, weakens and thus allows the elastomeric member to recover.

Heat-shrinkable sleeves find many applications, especially in the connection and termination of wires, cables and pipes. However, there are other applications where it is desirable to provide a connecting, insulating or protective heat-recoverable member for elongate objects such as cables and pipes where the ends are not accessible or, if they are accessible, where it is undesirable to disconnect or otherwise displace them. For such applications so-called "wrap-around" sleeves have been developed. Basically these are heat-recoverable sheets which can be wrapped round the substrate to form a generally tubular shape and which, in general, are provided with fastening means for holding them in the wrapped-up configuration during recovery. Typically such fastening means are mechanical in nature and comprise, for example, rigid clamps, pins or channel members which co-operate with suitably shaped moulded or extruded protuberances adjacent to the overlapping edges of the heat-recoverable sheet. Various types of fastening means are described for example in U.S. Patents 3,379,218 and British Patents 1,155,470; 1,211,988 and 1,346,479. In other applications, however, the sheet may be held in the wrapped-up configuration during recovery by means of an adhesive which may, in some cases, be applied on site.

Such heat-recoverable sleeves and wrap-around sleeves have been used for many applications including the protection against corrosion of metal substrates such as steel pipelines and the lead sheaths of electric cables. However, until now such heat-recoverable products have relied for their successful operation on their ability physically to prevent the hostile environmental components from contacting the metal surface. The present invention is based on our surprising observation that heat-recoverable products may be employed so as to prevent or reduce corroson both chemically and electrochemically as well as by physical isolation.

In its broadest form, the present invention provides a method of protecting a metal substrate against corrosion, which comprises causing a heat-recoverable member to recover about the substrate, a coating or lining of a sealant being positioned in the direction of recovery of the heat-recoverable member, which coating or lining contains a corrosion-inhibitor appropriate to the substrate. Preferably the sealant is provided on the heat-recoverable member, but if desired the sealant may be applied to the substrate as a separate layer before recovery of the heat-recoverable member.

In particular, the invention provides a method of protecting a metal substrate against corrosion which comprises causing a heat-recoverable member to recover about the substrate, a coating or lining of a sealant being positioned in the direction of recovery of the heat-recoverable member, which coating or lining contains a corrosion-inhibitor which is capable of passivating the surface of the metal substrate.

The present invention also provides a heat-recoverable article, especially a tubular sleeve, wrap-around sleeve, boot or end cap, suitable for use in such methods, the article comprising a heat-recoverable member which is provided, in the direction of recovery thereof, with a coating or lining of a sealant containing a soluble, passivating corrosion-inhibitor.

Two applications in which the present invention finds special utility are in the prevention of stress corrosion and in the reduction of cathodic disbonding, especially in the field of cathodic protection against corrosion.

Stress corrosion is a crack propagation effect caused by corrosion in members, especially metal, e.g. steel, structural members which are subjected to an external stress or which are left under a residual stress. The metal failure caused by corrosion in these circumstances is sometimes called stress corrosion cracking and is a major form of corrosion failure.

One particular field of concern is in the use of stress anchor bars, for example, in tunnel building and in road construction in mountainous areas.

In the latter, for instance where a road is being built along the side of a mountain, there is a danger that the mountain side above or below the road will collapse and destroy the road. To prevent cracks developing in the mountain side and subsequent rock falls the mountain is put under compression. This is achieved by stress anchoring.

Essentially the principle of stress anchoring is to embed metal bars at one end inside the mountain. Then the bars are stressed to about 80% of their yield strength and fastened while under tension to the mountain face. Thus the mountainside is in compression and cracks, etc. cannot occur or propagate themselves.

Stress anchor bars are of two general types:- ground anchor and rock anchor bars.

Ground anchor bars are typically 20 to 25 metres in length with diameters of 32 to 30 mm: the steel type used is generally 105/85 or similar. In drilling the length of hole required, the hole is somewhat helical. As a result a larger hole is drilled and a shell pipe fitted into it. The anchor rod is then contained within this shell pipe. The free length of the anchor bars, i.e. between the fixed anchor zone (in the mountain) and the anchor head (on the mountain face) must be corrosion protected. Stress corrosion of these bars is a major concern. Present systems use cement injection, i.e. grouting, or grease injection to protect the bar and keep adverse environments out from between the shell pipe and the bar.

The second type of bar, the rock anchor bars, are much shorter, only some 5 to 6 metres in length and with diameters of about 20 mm. The steel used is in general a lower yield strength steel such as 80/65. There is no shell pipe surrounding these and protection systems typically use epoxy coatings.

The main ground anchor corrosion protection systems suffer from the fact that they are injection systems. Complete covering of the bars is difficult because of possible air (and its associated moisture) entrapment and voids. These may be the source for causes of corrosion; the oxygen and moisture in the air pockets can set up a tiny corrosion cell because of inhomogeneities in the steel surface. Corrosion takes place, the moisture and oxygen being used up. With the difference in vapour pressures between the inside and the outside of the moisture and oxygen there is a diffusion of these into the pocket adding fuel to the corrosion process, and so-called "permeation corrosion" occurs. Furthermore any cracking of the cement protection, e.g. because of ground movement or vibration, can lead to moisture ingress and hence corrosion. In the rock anchors the epoxy coating can be readily damaged in field handling conditions.

In accordance with the present invention, however, the ground anchor or rock anchor bars may be protected by means of a heat-shrinkable sleeve on site immediately before they are installed in the mountain. Thus damage in handling is minimized and, in any case, the bars may readily be visually inspected for damage before installation.

In such an application both the sealant, e.g. the mastic or the adhesive, and the corrosion-inhibitor and the various components of the heat-recoverable member (e.g. any cross-linking agents employed) should preferably be free from halide, sulphur or nitrate moieties, e.g. ions, because these moieties may themselves induce stress corrosion. In addition, for any application, the sealant should have good wetting characteristics for the substrate so that the danger of entrapped air and subsequent permeation corrosion is avoided.

Sealants other than hot-melt adhesives are preferred because of their lower water vapour transmission, and mastics, particularly mastics based on polyisobutylene have been found to be especially effective for use in accordance with the invention. Because of the need for good flow and wetting characteristics the viscosity of the sealant is important and preferably lies between 100 poise and 2000 poise, especially from 200 to 600 poise at 160°C. Thus although, as is known, it is desirable to add a filler to reduce the cost of the sealant, the amount which can be added is limited by the need for a suitable viscosity. In general the maximum acceptable filler loading will be 30% by weight, typically useful fillers being calcium carbonate, wood flour, talc and mica.

The sealant may contain one or more tackifiers advantageously in an amount of up to 50 parts by weight, preferably from 5 to 40 parts by weight, especially from 10 to 20 parts by weight in order to ensure that the adhesion properties, especially to metal and polar substrates, are maintained. Aromatic tackifier are especially preferred for their temperature stability. Suitable tackifiers include, for example, terpene phenol resins, for example Piccofyn A100 (ex Hercules Incorporated), hydrocarbon resins, for example Escorez 1102 (ex Exxon Corp.), resin derivatives, for example Staybelite ester 10 (ex Hercules Inc.), chlorinated biphenyls, for example Arochlor 1254 (ex Monsanto Corp.), wood resins, for example Vinsol (ex Hercules Inc.) and polyketone resins. Some of these and other suitable tackifiers are described in German Offenlegungsschrift 23 47 779. Terpene phenol resins are particularly preferred. Other suitable materials will be apparent to those in the art.

The corrosion-inhibiting compound, from now on called the corrosion-inhibitor, will, of course, be chosen according to the nature of the metal of the substrate and the other requirements of the application. The loading must be sufficient to give protection (usually at least 0.5% by weight) but, in general should not be so great as to cause an undesired increase in viscosity (see above), the maximum loading preferably being typically about 25% by weight.

Corrosion inhibitors for various metals are, of course, well known and include, for example, phosphates, hydrogen phosphates, nitrites, nitrates, sulphates, chromates and silicates of the alkali metals, the alkaline earth metals, zinc and lead; iron oxide and red lead; calcium plumbate; silanes and amino-silanes; organic phosphates; ortho-nitrophenol; 2-nitrothiophene, alkoxyacetic acid, alkyl imidazolines, alkyl guanidines, alkyl morpholines; volatile amine salts of fatty acids such as dicyclohexyl ammonium palmitate; organic nitrites such as diisopropylamine nitrite; volatile amine carboxylates such as 2-butylamine benzoate; alkanoic acids, aromatic mono-carboxylic acids and triazoles. These and many other corrosion inhibitors are described, for example, in British Patents 1,370,204; 1,498, 175; 915, 512 and 904,861; and U.S. Patents 3,578,615; 3,730,937 and 3,080,211, the disclosures of which are incorporated by reference herein.

As is known, these corrosion inhibitors work by a variety of mechanisms, mainly by inhibiting the anodic and cathodic reactions which are primarily responsible for corrosion. So-called anodic inhibitors inhibit the anodic dissolution reaction, e.g., for iron,

$$Fe \rightarrow Fe^{++} + 2e \cdot$$

Amongst anodic inhibitors which may be used in the present invention there may be mentioned, for example, certain nitrites, chromates and molybdates (which form oxidising anions) and certain non-oxidizing anions containing oxygen, e.g. phosphates, tungstates and silicates. Amongst cathodic inhibitors which may be used there may be mentioned, for example, magnesium and calcium salts, which form relatively insoluble protective hydroxide films. In addition, certain inhibitors, e.g., polyphosphates, are thought to function by virtue of their interference with both the anodic and cathodic corrosion reactions.

The corrosion inhibitors preferred for use in most applications of the present invention are water-soluble to an appreciable extent and are preferably of low density so that they can be used to occupy a large volume in the sealant without adversely affecting the viscosity of the sealant.

In certain applications it will also be preferred that the corrosion inhibitor should not be one which produces excessively alkaline conditions in preventing corrosion. For example, as explained in U.S. Patent 3,730,937, whilst sodium and potassium chromate produce NaOH and KOH at cathodic sites which for certain metals, e.g. aluminium, may actually accelerate corrosion, magnesium chromate provides both cathodic inhibition (by the Mg^{++} ions) and anodic inhibition (by the chromate ions) without generating alkaline conditions.

The need to avoid excess alkalinity is thought to be especially important in a second major application of the present invention, namely in the suppression of cathodic dibonding where cathodic protection of the metal substrate is employed.

Underground structures have typically been protected against corrosion by the application of protective coatings. However, more recently, the method of cathodic protection has been employed and it is rapidly becoming a very important method. Basically, cathodic protection comprises imposing an electromotive force (EMF) on the structure so that it becomes cathodic in relation to the surrounding environment, e.g. the soil. This may be achieved by using auxiliary anodes to impose the EMF on the structure or by the use of so-called sacrificial anodes, corrosion of the structure being prevented by degradation of the anodes.

However, cathodic protection is rarely used alone as the current required would be very large and would tend to produce excessive alkalinity. In addition, it cannot prevent purely chemical corrosive attacks. The concurrent use of non-conducting adhering coverings has also been proposed but is unfortunately also relatively ineffective because the applied voltage promotes disbonding of the adhesive from the steel at the end of the coating or at places where the covering has been accidentally damaged and the steel exposed. This is undesirable as it increases the current required to maintain adequate cathodic protection.

It is therefore an important function of a protective composition not only that it reduces corrosion but also that it remains effective under various electrochemical strains and does not disbond from or cause other components to disbond from the substrate it is meant to protect.

We have found that cathodic disbonding is especially likely to occur in alkaline conditions and thus, in this further preferred application of the present invention the corrosion inhibitor is one which does not form an alkali in the potentially corrosive environment. Thus, preliminary tests have shown the need, in this application, to avoid the use of corrosion inhibitors which produce a high pH, for example of 14 or greater, with hydroxyl ions.

In one preferred aspect of the present invention there is provided a method of protecting a metal structure against corrosion which comprises applying a small negative electrical potential to the structure and protecting the structure by using a heat-recoverable member and, positioned between the heat-recoverable member and the metal structure, a coating or lining of a sealant composition containing a corrosion-inhibitor appropriate to the metal.

Corrosion inhibitors which are capable of giving passivating solutions are among those preferred for use in accordance with the invention.

It follows from the above that the corrosion inhibitor chosen will vary according to the particular application but that, for the presently preferred applications, the corrosion inhibitor will advantageously

(a) be one that does not produce alkaline materials, e.g. NaOH or KoH, in operation;
(b) be water soluble in an aqueous corrosive medium; and
(c) have a relatively low density.

For both the above specific applications of the present invention, the following are among the preferred corrosion inhibitors:

dicyclohexyl-ammonium nitrite;
zinc chromate;
zinc orthophosphate;
strontium orthophosphate;
sodium chromate;
sodium molybdate;
sodium nitrite;
sodium benzoate;
trisodium orthophosphate;
potassium dihydrogen orthophosphate;
disodium hydrogen orthophosphate;
magnesium hydrogen orthophosphate;
magnesium chromate.

The heat-recoverable member may be made from any of the polymers known from the art to be useful for the production of heat-recoverable articles. Generally the sheet material will be of constant composition throughout: however laminates of two different polymers bonded or fused together may be used in certain instances. Amongst suitable polymers there may be mentioned, for example, polyolefins, especially polyethylene, copolymers of ethylene and vinyl acetate, copolymers of ethylene and ethyl acrylate: chlorinated and fluorinated polymers, especially polyvinyl chloride, polyvinylidene fluoride and polymers incorporating units from vinylidene fluoride, hexafluoroethylene and chlorotrifluoroethylene: and rubbers such as ethylene/propylene rubber, chlorinated rubbers, e.g. Neoprene, and silicone rubbers which may be used in a blend with a crystalline or glassy polymer such as an olefin polymer. All of the above materials may, if desired, be cross-linked for example by irradiation and/or chemical means.

As mentioned above, a coating or lining of a sealant which contains a corrosion inhibitor is positioned between the heat-recoverable member and the substrate. The sealant may be, for example, a hot-melt adhesive. Especially suitable hot-melt adhesives include, for example, polyamides, ethylene/vinyl acetate copolymers and terpolymers (with or without incorporated waxes) and polyesters. Such materials are described, for example, in British Patent 1,440,810 and German OS 2,709,717. Also suitable in some applications are curable adhesives which melt and flow on heating but which will not afterwards be hot-meltable; amongst such materials there may be mentioned epoxy resins.

In many applications, however, the sealant is preferably a mastic, for example a mastic based on suitably modified butyl and isobutylene rubbers. The term "mastic" as used herein includes, amongst others, viscid, water resistant macromolecular compositions which exhibit both viscous and elastic response to stress. These materials are generally "monotonic", i.e. they do not undergo any signficantly abrupt decrease in viscosity upon heating to, for example, 300°C.

The mastics are preferably "tacky" at room temperature, that is, they are capable of forming an adhesive bond of measurable strength immediately after adhesive and the metal substrate are brought into contact under low pressure (cf. I. Skeist, Handbook of Adhesives, Reinhold Publishing Co. (1962)).

The properties of a mastic material are generally not predominantly attributable to any single component, but instead arise from the presence of a plurality of ingredients, usually including at least one rubbery material and one or more tackifying agents. Mastic materials may also contain, in particular cases, particulate fillers such as carbon black, asphaltic or other extenders and plasticizers, for example those well known to those skilled in the art.

Amongst suitable elastomers from which the sealants used in the present invention can be formulated there may be mentioned, for example, polyisobutylenes, for example the medium molecular weight (c. 80,000 - 100,000) material sold by Exxon Corporation under the name Vistanex L-80, ethylenepropylene terpolymer rubbers, for example those available from E. I. du Pont de Nemours & Co., Inc. under the name Nordel 1070E, and rubber reclaim compositions, for example that sold as 5496-F by Farboil Division, Beatrice Foods, Inc.. "Nordel" is a trade mark Amorphous, rubbery polyalkyl (e.g. C_4 or greater) methacrylates may also be employed.

As indicated above, the mastic may comprise one or more tackifiers depending upon the molecular weight of other mastic components and the temperature at which the articles, in a particular application, show advantages by aggressive tackiness. Especially where the rubbery component of the mastic exhibits a molecular weight substantially greater than 50,000, effective tackifying amounts of tackifiers are preferably employed. Preferred tackifiers include, as indicated above, terpene phenols (for example those available from Schenectady Chem. Corporation, as SP-553 and SP-559) and Piccopale 100 SF (Hercules Chemical Corporation), a cyclic, non-aromatic thermoplastic hydrocarbon resin resulting from polymerization of unsaturates obtained from deep-cracking of petroleum.

Some rubbery mastic components not otherwise tackified or tacky at room temperature become so as a result of scission induced by irradiation to crosslink the matrix material. Among rubbery mastic components in which scission predominates upon exposure to ionising radiation may be mentioned butyl rubbers; poly(vinyl alkyl ethers); amorphous, rubbery polyalkyl (e.g. C_4 or greater alkyl) methacrylates, and amorphous plasticized polyvinyl formals and butyrals.

The thickness of the sealant layer before recovery will, in general, be at least 1 mm.

Whilst the foregoing discussion has especially been directed to the problem of corrosion of steel substrates and, in one instance, to the problem of cathodic disbonding to steel substrates, it will be appreciated that the present invention is applicable to other metal substrates, for example, to lead substrates such as the sheaths of power cables etc. In this respect it will be noted that the rather unusual corrosion properties of lead are determined to a large extent by the low solubility of many of its salts and by its amphoteric nature (these properties being shared to a greater or lesser extent by zinc, copper, tin, cadmium, magnesium and nickel). Thus corrosion is accelerated by certain acids and alkalies, and is generally at a minimum within the pH range of from 6 to 9. Thus silicates, carbonates, sulphates, phosphates and certain organic compounds form suitable corrosion inhibitors. Other suitable compounds act to provide passivity or as buffers to keep the pH within the range of from 6 to 9.

The following Examples illustrate the invention. Parts and percentages are by weight unless otherwise indicated

Example 1

Stress anchor bars were protected by a heat-shrinkable sleeve provided with an inner layer of sealant/corrosion inhibitor and, in accordance with DIN 500 21, were subjected to a salt spray for up to 40 days. The protective sleeving was then removed and each bar was examined for spots formed by permeation corrosion. An examination for disbonding was made by cutting a slit 25 mm × 2 mm from the sleeve prior to testing and investigating the disbonding around the slit after the test. Typical specifications require this to be less than 5 mm from the lines of cutting.

The following formulations were evaluated, parts being by weight:-

Formulation	Sealant	Corrosion Inhibitor	Other Filler(s)	Tackifier
A	Vistanex LMMH 100 parts (Polyisobutylene)	$Zn_3(PO_4)_2$: 50 parts	-	Piccofyn: 30 A100 parts
B	Vistanex LMMH 100 parts	$Zn_3(PO_4)_2$: 25 parts	Zn dust 25 parts	Piccofyn: A100 30 parts
C	Vistanex LMMH 100 parts	$Zn_3 (PO_4)_2$: 50 parts	Carbon Black 1 part	Piccofyn A100 30 parts
D	Vistanex LMMH 100 parts	basic lead carbonate 20 parts	-	-
E	Vistanex LMMH 100 parts	basic lead carbonate 20 parts	Carbon black 1 part	Piccofyn A100 30 parts
F (comparative)	Lupolen 2810 100 parts		Hoechst E wax 100 parts Norsalone N2010 100 parts	Piccofyn A100 100 parts
G	Vistanex LMMH 100 parts	basic lead carbonate 5 parts	Carbon black 1 Whiting G400 ($CaCO_3$) 20 parts	Piccofyn: A100 30 parts
H	Vistanex LMMH 100 parts	basic lead carbonate 20 parts	Carbon black 1 part Wood flour 25 parts	-
I (comparative)	Vistanex LMMH 100 parts	-	-	Piccofyn A100 30 parts
J	Vistanex LMMH 100 parts	Basic lead carbonate 5 parts	-	Piccofyn A100 30 parts

"Lupolen" is a trade mark.

The results are summarised in Table I, together with results for various commercial sealants not including corrosion inhibitors. The table also contains some results obtained by salt dipping to effect contamination. It will be seen that formulations A to E, G, H and J containing corrosion inhibitors in accordance with the present invention gave much better protection against corrosion than sealants F and I.

[Where two or three samples were tested for any formulation, the results are marked (a), (b) etc.]

TABLE I

Adhesive	SALT DIPPING			SALT SPRAY		Disbonded area
	Days	Corrosion		Days	Corrosion	(mm)
A	44	Few isolated spots		18	Few spots on threads	42 × 8
B	44	Few spots on threads at ends of the sleeve		18	Few spots on threads	31 × 6
C	44	none		18	Few spots on threads	38 × 14
D	40	none		18	none	5 × 2
E	28	Few isolated spots	a)	18	none	4 × 4
			b)	18	Few spots in air gaps	6 × 3
			c)	18	Few spots in air gaps + isolated spots on threads	26 × 9
F				18	severe corrosion	total
G	23	corrosion on threads	a)	16	none	17 × 4
			b)	16	spots on threads	14 × 4

Adhesive	SALT DIPPING			SALT SPRAY		Disbonded area
	Days	Corrosion		Days	Corrosion	(mm)
H	23	none	a)	16	none	5 × 1
			b)	16	Few isolated spots	14 × 6
I	35	severe corrosion	a)	16	severe corrosion	22 × 9
			b)	16	severe corrosion	
I	23	severe corrosion	a)	16	severe corrosion	
$PbCO_3$	primer		b)	16	severe corrosion	
J	35	isolated spots on threads				
S 101 1	23	slight corrosion		16	erosion	36 × 19
				16	erosion	39 × 21
S 1052+ Rustban	36	severe corrosion				
S 1052+ Lanolene	36	severe corrosion, large spots in air enclosures				

"Rustban" is a trade mark

Example 2

This Example illustrates various sealant compositions suitable for use in the present invention.

Samples were prepared by pressing sealant formulations as indicated below onto 6″ × 3″ freshly grit-blasted steel plates at 80°C. The sealant layer were approximately 0.065″ thick.

A T-shaped piece was cut away from the top of each plate, the width of the 'T'-shaped piece being 5/16″. The sepeimens were put in a salt fog and were then investigated for corrosion and disbonding.

Formulations

	A	B
Vistanex LMMH	300	300
Piccofyn A110	90	90
Inhibitor	60	15

The following corrosion inhibitors were tested in both formulations A and B.

Dicyclohexyl ammonium nitrite
Zinc chromate
Zinc orthophosphate
Magnesium hydrogen orthophosphate
Strontium orthophosphate
Sodium chromate
Sodium molybdate
Sodium nitrite
Sodium benzoate
Potassium dihydrogen orthophosphate (38%))
Di-sodium hydrogen orthophosphate (62%))
Trisodium orthophosphate
All these inhibitors were found to give satisfactory results.

Other suitable testing methods are set out in ASTM-G8, ASTM-G42 and ASTM-G19.

Example 3

Cathodic disbonding tests were carried out at room temperature on various sealants which were provided as inner coatings on a heat-shrinkable sleeve (TPS sold by Raychem Corporation). The formulations comprised 47% polyisobutylene, 47% atactic polypropylene wax, and 6% of the corrosion inhibitors listed below. A comparative sample contained 6 parts carbon black in place of the corrosion inhibitor. The results are given in Table II along with data on the solubility of the inhibitors in water.

The test was carried out by shrinking the sleeves about a cathode in the form of a 50mm diameter grit-blasted steel pipe and the sealant was exposed at three points by drilling 9.5 mm diameter holes through the sleeve and sealant. The anode was a carbon rod. The electrolyte was 1% sodium chloride plus 1% sodium sulphate plus 1% sodium carbonate in distilled water. The protected cathode was maintained at - 1.5V with reference to a saturated calomel electrode for a period of 30 days then the average diameter of the disbonded area around the holes was measured. The general procedure was as set out in ASTM methods G8 and G42.

It will be seen from the table that several of the inhibitors markedly increased resistance to disbonding. Insoluble inhibitors were substantially ineffective, suggesting that to be effective the inhibitor must dissolve in the water diffusing through the adhesive and thereby be transported to the steel surface. Too high a solubility may ultimately be detrimental due to leaching out of the inhibitor by the electrolyte but, compared with inhibitors in paint formulations, this may be far less of a problem due to the much greater thickness of the adhesive compared with a paint film, and the extra protection afforded by the sleeve or similar superstrate. The utilisation of soluble or slightly soluble inhibitors is therefore preferred.

TABLE II

Inhibitor	Solubility	Disbonded diameter
Dicyclohexyl ammonium nitrite	slightly soluble	50 mm
$ZnCrO_4$	relatively insoluble	42 mm
$Zn_3(PO_4)_2\ 4H_2O$	-ditto-	55 mm
$MgHPO_4\ 3H_2O$	c 0.3g/100cc(20°C)	21 mm
$Sr_3(PO_4)_2$	relatively insoluble	40 mm
Na_2CrO_4	87g/100cc(30°C)	16 mm
$Na_2MoO_4 \cdot 2H_2O$	56g/100cc(0°C)	26 mm
$NaNO_2$	82g/100cc(15°C)	21 mm
$NaOOC \cdot C_6H_5$	66g/100cc(20°C)	25 mm
$KH_2PO_4(38\%)$	33g/100cc(25°)	23 mm
$Na_2HPO_4(62\%)$	c 100g/100cc(50°C)	
$Na_3PO_4 \cdot 4H_2O$	8.8g/100cc(20°C)	21 mm
Carbon black (comparison)		48 mm

Specification 1,081,291 describes a pressure sensitive adhesive containing, *inter alia*, hydrated calcium silicate coated on a biaxially oriented polypropylene film having a thickness of 0.00065 in. No claim is made herein to an article comprising a 0.00065 in. thick biaxially oriented polypropylene film having thereon a coating of a pressure sensitive adhesive containing hydrated calcium silicate.

WHAT WE CLAIM IS:-

1. A method of protecting a metal substrate against corrosion, which comprises causing a heat-recoverable member to recover about the substrate, a coating or lining of a sealant being positioned in the direction of recovery of the heat-recoverable member, which coating or lining contains a corrosion-inhibitor appropriate to the substrate.

2. A method as claimed in claim 1, wherein the corrosion-inhibitor is soluble.

3. A method as claimed in claim 1 or claim 2, wherein the corrosion-inhibitor is one which is capable of passivating the surface of the metal substrate.

4. A method of protecting a metal substrate against corrosion which comprises causing a heat-recoverable member to recover about the substrate, a coating or lining of a sealant being positioned in the direction of recovery of the heat-recoverable member, which coating or lining contains a corrosion-inhibitor which is capable of passivating the surface of the metal substrate.

5. A method as claimed in any one of claims 1 to 4, wherein the heat-recoverable member is heat-shrinkable.

6. A method as claimed in any one of claims 1 to 5, wherein the sealant is provided as a

coating or lining on the heat-recoverable member.

7. A method as claimed in any one of claims 1 to 5, wherein the sealant is applied to the substrate as a separate layer before recovery of the heat-recoverable member.

8. A method as claimed in any one of claims 1 to 7, wherein the heat-recoverable member is a sleeve, wrap-around sleeve, boot or end-cap.

9. A method as claimed in any one of claims 1 to 8, wherein the corrosion-inhibitor is a particulate solid which is dispersed in the sealant.

10. A method as claimed in any one of claims 1 to 9, wherein the corrosion-inhibitor is present in an amount of from 0.5 to 25% by weight based on the total weight of the coating or lining.

11. A method as claimed in any one of claims 1 to 10, wherein the corrosion-inhibitor is selected from chromates, molybdates, nitrites, phosphates, tungstates, silicates, and benzoates of the alkali and alkaline earth metals and zinc.

12. A method as claimed in any one of claims 1 to 10, wherein the metal substrate is iron or steel and the corrosion-inhibitor is selected from sodium chromate, sodium molybdate, sodium nitrite, sodium benzoate, trisodium orthophosphate, potassium dihydrogen orthophosphate, disodium hydrogen orthophosphate, magnesium hydrogen orthophosphate, magnesium chromate, and zinc chromate.

13. A method as claimed in any one of claims 1 to 10, wherein the metal substrate is lead and the corrosion-inhibitor is selected from silicates, carbonates, sulphates and phosphates.

14. A method as claimed in any one of claims 1 to 13, wherein the corrosion-inhibitor is at least partially ionizable in water.

15. A method as claimed in any one of claims 1 to 14, wherein the sealant comprises a filler.

16. A method as claimed in claim 15, wherein the filler is mica.

17. A method as claimed in claim 15, wherein the filler is talc.

18. A method as claimed in any one of claims 1 to 17, wherein the sealant is a mastic.

19. A method as claimed in claim 18, wherein the sealant is based on polyisobutylene, an ethylene propylene terpolymer or a butyl rubber.

20. A method as claimed in any one of claims 1 to 19, wherein the sealant comprises a tackifier.

21. A method as claimed in claim 20, wherein the tackifier is a terpene/phenol.

22. A method as claimed in any one of claims 1 to 21, wherein the sealant is a hot-melt adhesive.

23. A method as claimed in any one of claims 1 to 21, wherein the sealant is an epoxy resin.

24. A method as claimed in any one of claims 1 to 23, wherein the viscosity of the sealant is in the range of from 100 to 2000 poise at 160°C.

25. A method as claimed in claim 24, wherein the viscosity of the sealant is in the range of from 200 to 600 poise at 160°C.

26. A method as claimed in any one of claims 1 to 25, wherein the thickness of the sealant coating or lining is at least 1 mm.

27. A method as claimed in any one of claims 1 to 26, wherein a small negative electrical potential is applied to the metal substrate in order to provide cathodic protection against corrosion.

28. A method of protecting a metal structure against corrosion which comprises applying a small negative electrical potential to the structure and protecting the structure by using a heat-recoverable member and, positioned between the heat-recoverable member and the metal structure, a coating or lining of a sealant composition containing a corrosion-inhibitor appropriate to the metal.

29. A method as claimed in claim 27, wherein the corrosion-inhibitor is a soluble passivating inhibitor.

30. A method of protecting a stress anchor bar against corrosion which comprises covering it with a heat-shrinkable article provided with a coating or lining of a sealant composition containing a corrosion-inhibitor appropriate to the metal of the anchor bar and heating to cause the heat-shrinkable article to recover about the bar.

31. A method as claimed in claim 30, wherein the corrosion-inhibitor is a soluble compound capable of passivating the metal surface of the anchor bar.

32. A heat-recoverable article which is capable of protecting a metal surface against corrosion, the article comprising a heat-recoverable member which is provided, in the direction of recovery thereof, with a coating or lining of a sealant containing a soluble, passivating corrosion-inhibitor.

33. An article as claimed in claim 32, wherein the heat-recoverable article is heat-shrinkable.

34. An article as claimed in claim 32 or claim 33, wherein the heat-recoverable article is a sleeve, wrap-around sleeve, boot or end-cap.

35. An article as claimed in any one of claims 32 to 34, wherein the corrosion-inhibitor is a particulate solid which is dispersed in the sealant composition.

36. An article as claimed in any one of claims 32 to 35, wherein the corroson-inhibitor is present in an amount of from 0.5% to 25% by weight based on the total weight of the coating or lining.

37. An article as claimed in any one of claims 32 to 36, wherein the thickness of the coating or lining is at least 1 mm.

38. An article as claimed in any one of claims 32 to 37, wherein the corrosion-inhibitor is selected from chromates, molybdates, nitrites, phosphates, tungstates, silicates, and benzoates of the alkali and alkaline earth metals and zinc.

39. An article as claimed in any one of claims 32 to 37, wherein the corrosion-inhibitor is selected from sodium chromate, sodium molybdate, sodium nitrite, sodium benzoate, trisodium orthophosphate, potassium dihydrogen orthophosphate, disodium hydrogen orthophosphate, magnesium hydrogen orthophosphate, magnesium chromate, and zinc chromate.

40. An article as claimed in any one of claims 32 to 37, wherein the corrosion-inhibitor is selected from silicates, carbonates, sulphates, and phosphates.

41. An article as claimed in any one of claims 32 to 40, wherein the corrosion-inhibitor is at least partially ionizable in water.

42. An article as claimed in any one of claims 32 to 41, wherein the sealant comprises a filler.

43. An article as claimed in claim 42, wherein the filler is mica.

44. An article as claimed in claim 42, wherein the filler is talc.

45. An article as claimed in any one of claims 32 to 44, wherein the sealant is a mastic.

46. An article as claimed in claim 45, wherein the sealant is based on polyisobutylene, an ethylene-propylene terpolymer or a butyl rubber.

47. An article as claimed in any one of claims 32 to 46, wherein the sealant comprises a tackifier.

48. An article as claimed in claim 47, wherein the tackifier is a terpene/phenol.

49. An article as claimed in any one of claims 32 to 44, wherein the sealant is a hot-melt adhesive.

50. An article as claimed in any one of claims 32 to 44, wherein the sealant composition is an epoxy resin.

51. An article as claimed in any one of claims 32 to 50, wherein the viscosity of the sealant is in the range of from 100 to 2000 poise at 160°C.

52. An article as claimed in claim 51, wherein the viscosity of the sealant is in the range of from 200 to 600 poise at 160°C.

53. A method as claimed in claim 1 carried out substantially as described in any one of the Examples herein.

54. A heat-recoverable article as claimed in claim 32, substantially as described in any one of the Examples herein.

ABEL & IMRAY,
Chartered Patent Agents,
Northumberland House,
303-306 High Holborn,
London WC1V 7LH.

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