

Description

This invention relates to compositions suitable for the treatment of surfaces so as to provide water-erodible coatings thereon, to polymers for inclusion in the compositions, and to the treatment of surfaces using the compositions.

The problems caused by the adhesion of living organisms to surfaces, especially to surfaces subjected to an aqueous environment, are well known. An example is the fouling of underwater surfaces in, for example, the sea, rivers, lakes, canals, swimming pools, industrial plant, pipes, etc. This fouling is caused by the attachment to those surfaces of a variety of micro and other organisms which then grow and multiply so as eventually to cause a significant problem in relation to the surface concerned. Of particular importance is the case of a ship's hull; the growth of marine organisms thereon increases the frictional resistance of the hull to passage through water and so increases fuel consumption and/or reduces the speed of the ship. Removal of the growths by cleaning and repainting the ship's hull in a dry dock is extremely expensive and time-consuming.

Another example of the attachment of micro-organisms to a surface subjected to an aqueous environment is the adhesion of bacteria, for example *Streptococcus mutans*, to human teeth leading, in many cases, to dental caries or other oral hygiene problems.

One approach to these problems has been to use biocides (by "biocides" is meant herein substances which are toxic to and destroy various types of microorganisms, and include e.g. fungicides, algicides, etc). Thus, it is known to apply to ships' hulls antifouling coatings in which the active ingredient is a biocide which is slowly released from the coating over a period in sufficient concentration to be lethal to marine organisms in the immediate vicinity of the protected surface. Eventually, the concentration of biocide in the coating falls below the lethal concentration and the coating must be renewed. For a time, this method provides an effective means of reducing surface fouling.

An alternative development has been the use of the antifouling coatings in which an organic tin biocide compound is present as a hydrolysable group attached to the polymer backbone. Hydrolysis of these linkages releases toxic organotin material, leaving a water erodible polymer residue, which is subsequently removed by motion of the vessel through the sea-water. A fresh surface is thus revealed. Such action produces a "self-polishing" effect and increases fuel efficiency. In addition, release of organotin biocide is relatively constant during the lifetime of the coating.

A recent patent application (PCT Application WO 84/02915) discloses an antifouling coating comprising mixtures of biocides and erodible polymers of substituted acrylic and methacrylic esters. A number of hydrolytically unstable polymers have been described.

A different type of coating is described in Japanese Patent Publication No 78-108126. This document embodies a solvent-borne coating comprising a biocide (triphenyltin hydroxide) and a polymeric binder based on a copolymer of polypropylene glycol, methyl methacrylate, ethyl acrylate and vinyl acetate. Antifouling properties and excellent crack resistance are claimed, although inclusion of toxic material is still required.

The need for regular renewal of coatings which are not self-polishing is a disadvantage. Also the danger to the aqueous (marine) environment posed by the continuous release of toxic organotin groups from a polymer chain backbone by hydrolysis in a self-polishing action is now becoming apparent.

Another approach to this type of problem relies on the use of agents which are not toxic to the offending organisms but prevent or reduce their adhesion to the surface in question. An example of this approach in relation to the protection of ships' hulls is described in the Journal of Coatings Technology, 54, 83, 1982. Coatings made of cellulose acetate and silica-bearing methyl siloxane resin applied respectively to PVC and steel panels showed marine fouling resistance for a short period of time. According to the authors, no non-toxic anti-fouling coatings have reached a commercial stage.

Another example (Japanese Patent Publication No 78-97084) discloses a water-thinned coating composition based on polypropylene glycol methacrylate and a number of (meth)acrylic esters which is applied to steel and baked at 100°C, to give a coating which is more resistant to "soiling" than one in which polypropylene glycol monomethacrylate is absent.

A method of treating a rather different kind of marine substrate is described in Japanese Patent Publication No 77-81289 which is concerned with preventing the attachment of marine creatures to the surface of shellfish. The method comprises forming a water-swellaable polymer on the surface of the shell by polymerising a monomer thereon in the presence of an acidic sulphite ion and a peroxide. This document specifically describes the formation of a water-swellaable polymer on the shells of pearl oysters by the polymerisation of acrylamide together with a minor amount of methylene-bis-acrylamide. Other monomers mentioned include the polyethylene glycol and polypropylene glycol esters of acrylic and methacrylic acids,

vinyl pyrrolidone, vinyl pyridine and styrene sulphonic acid. In order for the polymer to be strongly held to the surface of the shell, the use of the acidic sulphite ion is essential.

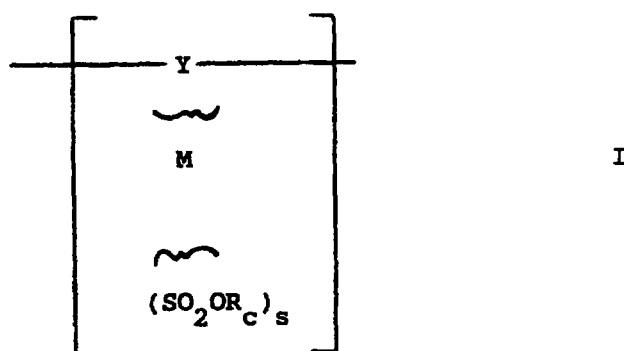
In the field of oral hygiene, attempts to prevent calculus and plaque from adhering to the surfaces of teeth have included the use of cationic, nonionic and anionic surface active agents (for example J. Periodont, 38, 294, 1967 and Caries Res. 16, 440, 1982). In general, the nonionic agents (usually polyethenoxy compounds) have been found less effective than the ionic surface active agents.

In our European Patent Publication No 0182523A and UK Publication No 2187075A we describe certain defined formulations containing polyethenoxy and polypropenoxy compounds. These compounds have shown efficacy in substantially reducing bacterial adherence to surfaces of teeth and reduction of bacterial growth on treated hydrophobic surfaces such as painted steel.

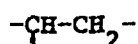
There has also been described (e.g. in German Offen. 2 601 928, PCT Application WO 80/00554, Japanese Patent Publication 85-65076, and German Offen. 3 322 470) the uses of non-toxic matrix coatings in which diffusion-controlled release of hydrocarbon and/or silicon oils are claimed as effective antifouling coatings. Diffusion-controlled oil release however suffers from the limitations of all matrix systems in that release is time dependent, exhausted films require treatment before recoating and, more importantly, the absence of a self-polishing effect.

The present invention is concerned with coating compositions for providing a surface with a water-erodible coating which comprise an erodible polymer as hereinafter defined comprising sulphonate ester groups, which groups generate acidic surface groups during hydrolysis thereby rendering the polymer and the coating containing it erodible; the non-sulphonate (i.e. alcoholic) residues may themselves optionally be hydrophobic in nature and so may function in an analogous way to the paraffin or silicon oil matrix system mentioned above, but with the advantage of time-independent release coupled with the above-mentioned self-polishing effect. A biocide(s), and particularly a non-tin based biocide, may be incorporated in combination with the erodible polymer into the polymer-containing coating to provide effective antifouling behaviour. Furthermore, the erodible polymer can optionally contain alkylene oxide or poly(alkylene oxide) groups therein to generate an anti-adhesive effect which may inhibit antifouling in its own right whereby the presence of a biocide may not always be necessary (although its use may still be preferred).

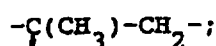
Accordingly, the present invention provides a coating composition suitable for treating a surface so as to provide a water-erodible coating thereon, which coating composition comprises at least one erodible polymer comprising 3 to 40 mole % of one or more repeat units A each comprising at least one hydrolysable sulphonate ester group pendant to the main chain backbone of the polymer, wherein said repeat unit A has the formula:



wherein Y, which in the repeat units A of Formula I may be the same or different, is a group in the main chain backbone selected from



and



s is an integer of 1 or more corresponding to the number of SO_2OR_c groups in repeat unit A of Formula I; R_c , which in the same repeat unit A of Formula I (when s is 2 or more) or in different repeat units A of Formula I may be the same or different, is a group selected from one or more of alkyl (including primary, secondary and tertiary alkyl and cycloalkyl), aryl, alkaryl, aralkyl, alkenoxyalkyl and poly(alkenoxy)alkyl groups;

and wherein each SO_2OR_c group is joined via an intermediary M to the group Y, M being a direct link or a group selected from $-(\text{alkylene})-$, $-\text{CO}-\text{O}-(\text{alkylene})-$, $-\text{CO}-\text{NH}-(\text{alkylene})-$, $-\text{NH}-\text{CO}-(\text{alkylene})-$, $-(\text{arylene})-$, $-(\text{alkylene})-(\text{arylene})-$, $-(\text{alkylene})-\text{O}-(\text{alkylene})-$, $-(\text{alkylene})-\text{O}-(\text{arylene})-$, $-(\text{arylene})-\text{O}-(\text{arylene})-$, $-(\text{arylene})-\text{O}-(\text{alkylene})-$, $-\text{alkylenoxy}-$, and $-\text{polyalkylenoxy}-$ groups.

Thus when a surface is coated using a composition according to the invention, the resulting dried coating is water-erodible in an aqueous environment by virtue of polymer-bound acid groups being formed from the sulphonate ester groups by hydrolysis, these being (at least for the most part) located on polymeric material in the environment-exposed exterior portion of the coating.

By a sulphonate ester group is meant a group or linkage of formula



As far as each individual sulphonate group is concerned, its location in the polymer may be represented by



where R_a and R_b are residues representing the remainder of the polymer in relation to each individual sulphonate. The hydrolysis of any sulphonate group in an aqueous environment (particularly in a marine environment of pH 8.1 to 8.3) can therefore be written as follows:



so that $-\text{SO}_2\text{OH}$ acid groups are formed bonded to polymeric residues of the polymer located (at least for the most part) at the environment exposed exterior portion of the applied coating. (It may be mentioned here that polymer-bound sulphate ester, which are not included within the scope of the invention, would be expected to hydrolyse in a similar manner). It may possibly be the case that these acid groups themselves inhibit the adhesion of living organisms to a certain extent; more importantly, however, they render water-erodible the polymeric residues to which they are attached so that an outer surface comprised of fresh unhydrolysed polymer molecules is continually formed, i.e. the polymer exhibits a "self-polishing" effect.

Thus, by an "erodible polymer" is meant a polymer having polymeric residues that are removable under the conditions of use to which the coated surface is subjected thereby rendering the coating itself erodible; this may involve simple dissolution in the aqueous environment but more usually involves relatively facile but slow removal thereof as a result of relative motion in the vicinity of the coated surface, e.g. by motion of the surface (being e.g. part of a vessel, e.g. a ship's hull) through water or by the passage of water over the stationery surface (being e.g. part of a water-conveying conduit or pipe). If the coating also contains a biocide, that portion of it associated with the polymer being released at the surface of the coating is also released at the same time into the aqueous environment thereby creating an anti-fouling action. As mentioned above, the polymer may itself contain groups which create an anti-adhesion effect which might render the need for biocide unnecessary.

Any suitable polymerisation technique may be used to form the erodible polymer, e.g. polymerisation by a free-radical or ionically initiated addition process. Free-radical addition processes (as used for olefinically unsaturated monomers) are normally employed.

The erodible polymer comprises 3 to 40 mole % of repeat units A, more preferably 3 to 30 mole % (with 5 to 20 mole % being a typical range). The presence of higher levels of repeat units A in the polymer may in some cases render the resulting coating rather too erodible and liable to break up fairly quickly.

The repeat units A in the polymer will usually all be of the same specific structure, although the scope of the invention is intended to embrace polymers having repeating units A of more than one specific structure.

In repeat unit A of Formula I, the intermediary M (which it will be appreciated may be the same or different in the repeat units A) is a direct link (this is to say a direct bond) or a group selected from:

- certain aliphatic groups, viz. - certain carboxylic ester groups, viz.	-(alkylene)- -CO-O-(alkylene)-
- certain carboxylic amide groups, viz.	-CO-NH-(alkylene)- or -NH-CO-(alkylene)-
- certain aromatic groups, viz. - certain alkarylene groups, viz.	-(arylene)- -(alkylene)-(arylene)-
- certain ether groups, viz.	-(alkylene)-O-(alkylene)- -(alkylene)-O-(arylene)- -(arylene)-O-(arylene)- -(arylene)-O-(alkylene)-
- alkyleneoxy or poly(alkyleneoxy) groups.	
(N.B. in the above groups, the far right hand bond is intended to represent a bond to the sulphonate group).	

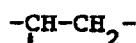
In the above-mentioned possibilities for M, the -(alkylene)- groups can provide a linking chain of 1 or more carbon atoms, e.g. 1 to 20 carbon atoms (when more than about 20 carbon atoms exist between the hydrolysable pendant sulphonate group and the polymer backbone, the contribution to the erodibility of the polymer by this group might become rather weak and so might not be very useful). Hence the preferred -(alkylene)- groups can be represented by $-(CR_1R_2)_n-$ where n is an integer of 1 to 20 and R_1 and R_2 (which may be the same or different in each or, when n is 2 or more, in different $-CR_1R_2-$ groups of the -(alkylene)-chain) are selected from H and alkyl or substituted alkyl groups (more preferably H or lower alkyl of 1 to 5 carbon atoms, particularly methyl, groups). Examples of such preferred alkylene groups would e.g. be $-(CH_2)_n-$ where n is e.g. 1 to 20. Substantially the same considerations apply to the more hydrophilic alkyleneoxy or polyalkyleneoxy groups, with preferred groups of this type being represented by $-(CHR_3CHR_4O)_m-$ where m is e.g. 1 to 15 and R_3 and R_4 (which may be the same or different in each $-CHR_3CHR_4O-$ unit) are selected from H and alkyl or substituted alkyl (more preferably, H or lower alkyl of 1 to 5 carbon atoms, particularly methyl). Examples of such preferred alkyleneoxy groups would be $-(CH_2CH_2O)_m-$ and $-(CH_2CH(CH_3)O)_m-$ where m is, e.g. 1 to 15. The -(arylene)- groups in the above mentioned possibilities for M can be represented by divalent aromatic radicals comprising a single or linked benzene ring system or conjugated benzene ring system (although conceivably heteroaromatic rings might also be utilised). Usually the arylene groups will be para phenylene (ortho or meta phenylene can also be used). The use of para phenylene for M is particularly favoured since starting monomers (for making A repeat units) containing it are readily prepared.

In repeat unit A of Formula I the residue R_c may be selected to provide a desired hydrolysis rate, i.e. to provide a certain degree of control over the hydrolysis rate under the conditions of use. Also, as discussed above, if R_c is itself hydrophobic in nature, its release may well provide an additional degree of antifouling behaviour. Examples of R_c residues include one or more of the following groups:

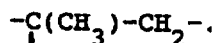
- alkyl groups such as those containing 1 to 20 carbon atoms (more preferably 1 to 15 carbon atoms), examples of which include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert.butyl, n-pentyl, n-hexyl, cyclohexyl and n-decyl;
- aryl groups such as phenyl;
- alkaryl or aralkyl groups such as benzyl;
- alkyleneoxyalkyl or poly(alkyleneoxy)alkyl groups such as $(CH_2CH_2O)_pCH_3$ or $(CH_2CH_2(CH_3)O)_pCH_3$ where p is 0 to 100.

Substituted derivatives of the above examples may of course also be used if appropriate (substituents could e.g. be halogen, hydroxy, alkoxy, aryl, alkyl and so on). We have found that control of the hydrolysis rate may indeed be controllable by appropriate selection of R_c and, interestingly, our results so far indicate that hydrolysis appears to proceed more quickly with increasing chain length in R_c in the R_c = lower alkyl series (the reverse might perhaps have been expected).

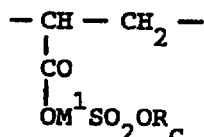
The group Y is selected from



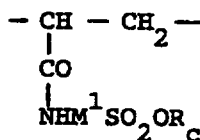
and



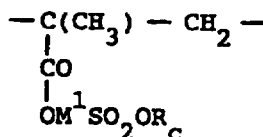
Thus, as an example, the repeat unit A of formula I might be derived from the polymerisation (usually free radical initiated) of an acrylic acid or methacrylic acid ester or amide formed from the reaction of acrylic or methacrylic acid, or an esterifiable or amidifiable derivative thereof such as an acid chloride or anhydride, and a hydroxy compound of formula $\text{HO-M}^1\text{-SO}_2\text{OR}_c$ (to form the ester) or an amine of formula $\text{H}_2\text{N-M}^1\text{-SO}_2\text{OR}_c$ (to form the amide) (where M^1 is an alkylene group). The acid used to form the ester or amide might e.g. be acrylic or methacrylic acid, giving rise to structures for A of:



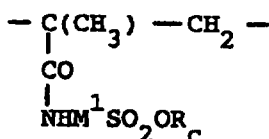
and



in the case of acrylic acid, and

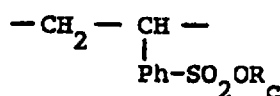


and

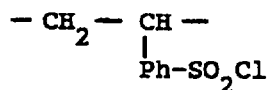


in the case of methacrylic where the links $-\text{COOM}^1-$ and $-\text{CONHM}^1-$ represent M.

Rather more simply, the repeat units A of formula I may be derived from the free-radical initiated polymerisation of an appropriately substituted olefine e.g. an olefine of formula $\text{CH}_2=\text{CHMSO}_2\text{OR}_c$ (where M is as defined herein) or a related compound $\text{CH}_2=\text{CHMSO}_2\text{G}$ where G is a group that is readily convertible to $-\text{OR}_c$ after polymerisation, and in particular is a halogen such as Cl (or Br) which may be easily converted to $-\text{OR}_c$ after polymerisation e.g. by reaction with an alkanol R_cOH . We have employed this technique extensively by employing as starting monomer for making repeat units A either styrene p-sulphonate esters ($\text{CH}_2=\text{CH-Ph-SO}_2\text{OR}_c$ where $-\text{Ph}-$ is para phenylene) or styrene p-sulphonyl chloride ($\text{CH}_2=\text{CH-Ph-SO}_2\text{Cl}$), the former yielding directly repeat units A of formula:

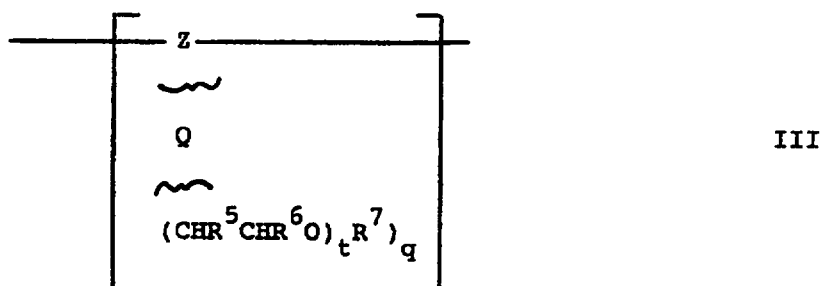


and the latter yielding repeat units A of formula:



which may be readily converted to the above-mentioned A units by esterification with R_cOH . In fact we prefer to proceed via the acid chloride in this system (see examples) because the styrene p-sulphonate esters themselves have tended to yield polymers of lower molecular weights and require repeated initiation to facilitate complete polymerisation whereas the acid chloride monomer polymerises smoothly to yield high molecular weight material.

If the polymer used in the coating composition of the invention contains alkylene oxide or poly(alkylene oxide) groups, this expedient will in itself provide a degree of antifouling (antiadhesive) behaviour for the coating in the same manner as described in European Patent Publication No.018523A and UK Patent Publication No.2167075A discussed hereinbefore. Such groups could e.g. comprise intermediary M or residue R_c in a repeat unit A of formula I. Additionally or alternatively such alkylene oxide or poly(alkylene oxide) groups could form part of other repeat units of the polymer not associated with a sulphonate group (as they are in repeat units A if they comprise intermediary M or residue R_c). Such additional or alternative alkylene oxide or poly(alkylene oxide)-containing repeat units, i.e. units not being associated with a sulphonate ester group (nor a sulphate ester group for that matter), are hereinafter termed repeat units C and have a formula as defined hereinafter. The erodible polymer of the coating composition preferably comprises 0 to 50 mole % (more preferably 0 to 40 mole % and particularly 0 to 30 mole %) of such repeat units C (and if used, preferably up to 50 mole %, more preferably up to 40 mole % and particularly up to 30 mole % of repeat units C) where the chain length of the polyalkylene oxide usually comprises 1 to 200 of such units. A repeat unit C has the formula:



wherein

t is an integer of from 1 to 200, preferably between 1 and 60 and particularly between 1 and 20;

q is an integer of from 1 to 4, preferably 1 or 2;

Z, which in the same repeating units C of formula III may be the same or different, is a hydrocarbyl residue or a substituted derivative thereof (providing part of the polymer backbone);

R^5 , which is the same repeating unit C of formula III (when t or q is two or more) or in different repeat units C of formula III may be the same or different, is hydrogen or methyl;

R^6 , which in the same repeat unit C of formula III (when t or q is 2 or more) or in different repeat unit C of formula III may be the same or different, is hydrogen or methyl;

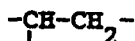
except that R^5 and R^6 in a single unit $(\text{CHR}^5\text{CHR}^6\text{O})$ cannot both be methyl;

R^7 , which in the same repeating unit C of formula III (when q is 2 or more) or in different repeating units C of formula III may be the same or different, is hydrogen or an alkyl group (e.g. a lower alkyl group

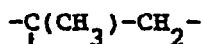
containing 1 to 5 carbon atoms such as methyl), or an acyl group;
 and wherein each $(\text{CHR}^5\text{CHR}^6\text{O})_t$ group is joined via an intermediary or intermediaries Q to the hydrocarbyl residue Z, and in cases where q is 2 to 4 may be joined by Q to the same or different carbon atoms of Z;
 and wherein Q represents one or more intermediaries and wherein Q may be the same or different in the
 5 repeat units C and is selected from one or more direct links and one or more atoms or groups of atoms providing a chain of one or more atoms for linking a $(\text{CHR}^5\text{CHR}^6\text{O})_t$ group with Z, except that more than two $(\text{CHR}^5\text{CHR}^6\text{O})_t$ groups cannot be directly linked to the same carbon atom in Z if that carbon atom forms part of the main chain polymer backbone.

10 In repeat unit C of formula III, each $(\text{CHR}^5\text{CHR}^6\text{O})_t$ group is joined to the hydrocarbyl residue Z by means of an intermediary or intermediaries (i.e. by a linking entity or entities), this or these being denoted by Q, which is selected from one or more direct links and one or more atoms or groups of atoms providing a chain of one or more atoms for linking a $(\text{CHR}^5\text{CHR}^6\text{O})_t$ group(s) with Z. Usually, Q does not contain a hydrolytically unstable linkage. In cases where q is 2 to 4, each $(\text{CHR}^5\text{CHR}^6\text{O})_t$ group may be joined by Q to the same or, in cases where Q represents more than one intermediary, to the same or different carbon
 15 atoms in Z, although more than two $(\text{CHR}^5\text{CHR}^6\text{O})_t$ groups cannot of course be directly linked to the same carbon atom of Z if that carbon atom forms part of the main chain polymer backbone. It will be noted that in principle Q can represent up to 4 separate intermediaries in repeat unit C (in cases where q is 4). Q may be the same or different in the repeat units C of formula III.

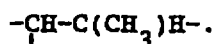
In repeat unit C of formula III, Z may e.g. be



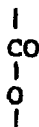
or alkyl substituted derivatives thereof (particularly lower alkyl of 1 to 5 carbon atoms such as methyl) e.g.



or



35 While Q may represent one or more direct links in repeat unit C of formula III, it is preferred in the present invention that Q is one or more atoms or groups of atoms providing a linking chain of one or more atoms; such a chain will normally comprise one or more carbon and/or hetero atoms (particularly N and/or O). Particularly preferred examples of linkages provided by Q are:



45 and



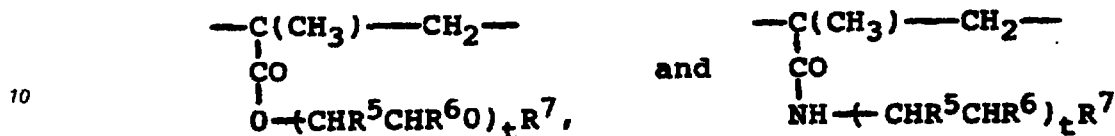
where the top bonds are to Z and the bottom bonds are to $(\text{CHR}^5\text{CHR}^6\text{O})_t$.

55 It is preferred in repeat unit C of formula III that q is 1 or 2 (so that Q can then represent one, or at most two intermediaries).

Preferably a repeat unit C of formula III is derived from the polymerisation (usually free-radical initiated) of a polymerisable olefinically unsaturated ester or amide formed from the reaction of an alpha, beta

unsaturated carboxylic acid (or an esterifiable or amidifiable derivative thereof such as an acid chloride or anhydride) and a hydroxy compound of formula $\text{HO}(\text{CHR}^5\text{CHR}^6\text{O})_t\text{R}^7$ (to form the ester) or an amine of formula $\text{H}_2\text{N}(\text{CHR}^5\text{CHR}^6\text{O})_t\text{R}^7$ (to form the amide). Preferably the acid used to form the ester or amide is acrylic or methacrylic acid, particularly the latter,

giving rise, respectively, to the following structures for C:



Repeat units C might also be formed by polymerisation of the alpha, beta unsaturated carboxylic acid itself (or an esterifiable derivative thereof such as an acid chloride), e.g. acrylic or methacrylic acid (or their acid chlorides), followed by esterification of the polymer acid groups (or acid chloride groups) with an alkylene oxide such as ethylene oxide or propylene oxide.

The repeating units C may alternatively be formed by the partial esterification or amidification of an already-polymerised olefinically unsaturated alpha, beta carboxylic acid (or an esterifiable or amidifiable derivative thereof such as an acid chloride or anhydride) using, preferably, an alcohol of formula $\text{HO}(\text{CHR}^5\text{CHR}^6\text{O})_t\text{R}^7$ or an amine of formula $\text{H}_2\text{N}(\text{CHR}^5\text{CHR}^6\text{O})_t\text{R}^7$. The remaining (unesterified or unamidified) carboxyl groups, if any, with their associated sections of the polymer backbone will of course provide acidic units of structure D (see later; the same of course applies to esterification with an alkylene oxide).

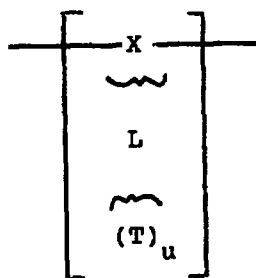
Normally the repeat units C (if present) will all be of the same specific structure, although the scope of the invention is intended to embrace polymers having repeat units C of more than one specific structure.

In repeat unit C of formula III, it is preferable that substantially both of the R^5 and R^6 groups may be hydrogen in which case $(\text{CHR}^5\text{CHR}^6\text{O})_t$ is $(\text{CH}_2\text{CH}_2\text{O})_t$. Alternatively one of R^5 and R^6 may be hydrogen and one methyl, giving rise to $(\text{CH}_2\text{C}(\text{CH}_3)\text{HO})_t$ or $(\text{CH}(\text{CH}_3)\text{CH}_2\text{O})_t$. Such groups may be derived from the alcohol $\text{HO}(\text{CHR}^5\text{CHR}^6\text{O})_t\text{R}^7$ or the corresponding amine $\text{H}_2\text{N}(\text{CHR}^5\text{CHR}^6\text{O})_t\text{R}^7$. Where a proportion of the R^5 and R^6 groups in the polymer are methyl, either all the R^5 or R^6 groups in one or more of the $(\text{CHR}^5\text{CHR}^6\text{O})_t$ chains may be methyl, or one or more (but not all) of the R^5 or R^6 groups in one or more of the $(\text{CHR}^5\text{CHR}^6\text{O})_t$ chains may be methyl. R^5 and R^6 should not, however, both be methyl in the same unit $(\text{CHR}^5\text{CHR}^6\text{O})_t$ as specified hereinbefore. Such a chain could for example be derived from an amine such as $\text{H}_2\text{N}[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}]_2(\text{CH}_2\text{CH}_2\text{O})_4\text{C}_4\text{H}_9$ (where CHR^5CHR^6 is $\text{CH}(\text{CH}_3)\text{CH}_2\text{O}$ and $\text{CH}_2\text{CH}_2\text{O}$, t is 6, and C_4H_9 is normal butyl), or other analogous amines (varying $\text{CHR}^5\text{CHR}^6\text{O}$ and t). It could also be derived from an alcohol, such as $\text{HOCH}(\text{CH}_3)\text{CH}_2\text{OR}^7$.

It should be appreciated that in many cases, repeat unit C of formula III will be derived from a polyalkenoxy monomer (particularly if obtained commercially) which may have a small spread of polyalkenoxy chain length so that, overall, n may represent an average value which is not a whole number (although strictly speaking n must be an integer in any specific polymer repeat unit). For example we have made polymers according to the invention derived from a polypropylene glycol monomethacrylate of average molecular weight 420, this being mainly an equal mixture of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2[\text{CH}_2\text{CH}(\text{CH}_3)]_5\text{CH}_3$ and $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2[\text{CH}_2\text{CH}(\text{CH}_3)]_6\text{CH}_3$ giving rise to corresponding repeat units C with $n = 5$ and $n = 6$ but with an overall (average) n value of about 5.5.

Preferably R^7 is a lower alkyl group containing 1 to 5 carbon atoms, e.g. n-butyl or (more preferably) methyl. It may, nevertheless, be hydrogen.

The erodible polymer used in the coating composition of the invention may also optionally comprise one or more repeat units which contain acidic and/or basic groups (other than those derivable from sulphonate hydrolysis in the polymer molecule, or sulphate ester hydrolysis for that matter). Such repeat units are hereinafter termed repeat units D and have a formula as defined hereinafter. The polymer of the coating composition of the invention preferably comprises 0 to 30 mole % more preferably 0 to 20 mole % and particularly 0 to 10 mole % of such repeat units D (and if present, preferably up to 30 mole %, more preferably up to 20 mole % and particularly up to 10 mole % of repeat units D). An acidic or basic repeat unit D has the formula:



IV

wherein X, which in the repeating unit D of formula IV may be the same or different, is a hydrocarbyl residue or a substituted derivative thereof (providing part of the polymer backbone);

u is an integer of 1 to 4;

T, which in the repeating units D of formula IV may be the same or different, is a group bearing an acidic or basic substituent (other than one derivable from sulphonate or sulphate ester hydrolysis);

and wherein each T group is joined via an intermediary or intermediaries L to the hydrocarbyl residue X, and in cases where u is 2 to 4 may be joined by L to the same or different carbon atoms of X; and

wherein L represents one or more intermediaries and wherein L may be the same or different in the repeat units D of formula IV and is selected from one or more direct links and one or more atoms or groups of atoms providing a chain of one or more atoms for linking a T group with X, except that more than two T groups cannot be directly linked to the same carbon atom in X if that carbon atom forms part of the main chain polymer backbone.

Preferably the repeat unit D represents the repeating unit derived from the polymerisation (usually free-radical initiated) of one or more polymerisable olefinically unsaturated monomers which bear a basic group, e.g. a tertiary amino group, or an acidic group, e.g. a carboxylic acid group. Examples of such carboxylic acid group-bearing monomers are acrylic acid, methacrylic acid, maleic (or fumaric) acid, itaconic acid, N-methacryloyl alanine, and N-acryloyl hydroxy glycine. An example of a tertiary amino-bearing unsaturated monomer is N,N-dimethyl-2-aminoethyl methacrylate. Preferred examples of monomers for yielding repeat units D at our present stage of knowledge are methacrylic acid, acrylic acid, maleic acid, and N,N-dimethyl-2-aminoethyl methacrylate. Usually, the repeating units D (if present) will all be of the same specific structure, although the scope of the invention is intended to embrace polymers having repeating units D of more than one specific structure.

The erodible polymer used in the coating composition of the invention besides comprising repeat units containing sulphonate ester groups denoted by A, and optionally repeating units C containing alkylene oxide or poly(alkylene oxide) groups, and optionally repeat units D containing acidic and/or basic groups, may also optionally comprise one or more other types of repeat unit(s). Such other repeat units, i.e. repeat units other than those containing sulphonate ester groups (or sulphate ester groups for that matter) or having the structures of repeat units C or D, are hereinafter collectively termed repeat units E (for convenience). The erodible polymer preferably comprises 5 to 97 mole % of repeat units E (more preferably 30 to 95 mole % of such units). Such other repeat units E may e.g. be provided by the free-radical addition polymerisation of one or more olefinically unsaturated monomers (different to those already mentioned hereinbefore and usually of a simpler, well-known type). Examples of monomers for free-radical addition polymerisation to form repeat units E include esters and amides of olefinically unsaturated carboxylic acids, e.g. acrylic or methacrylic acid esters (e.g. methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, acrylamide, methacrylamide, etc.), alpha aryl-substituted monoolefines (such as styrene or alpha methyl styrene), vinyl esters such as vinyl acetate, vinyl or vinylidene halides such as vinyl chloride and vinylidene chloride, and olefinically unsaturated nitriles such as acrylonitrile and methacrylonitrile.

Preferred erodible polymers in the coating compositions of the invention comprise 3 to 40 mole % of one or more repeat units A, 0 to 40 mole % of one or more repeat units C, 0 to 20 mole % of one or more repeat units D and 5 to 97 mole % of one or more repeat units E.

The erodible polymers used in the coating compositions of the invention need not be straight chain polymers, but may also be branched and/or (to a very small extent) cross-linkable.

It is to be understood that the definition of the erodible polymer (as given hereinbefore) is also intended to embrace a polymer in which at least some of the acidic or basic groups in the repeat units D, if present, have been converted to the corresponding salt anions or cations, e.g. CO_2^- in the case of CO_2H groups or quaternary ammonium cations in the case of amines (these still being considered as carboxyl or amino groups as far as the definition of D is concerned). Such a conversion could e.g. be effected as a result of

incorporating the polymer into an alkaline or acidic medium (respectively).

Typically the erodible polymers used in the coating composition of the invention have weight average molecular weights (M_w) within the range of from 5,000 to 500,000 (more usually 50,000 to 300,000), although we do not exclude the possibility that suitable erodible polymers having molecular weights outside this range may be used in the present invention.

It is believed that the erodible polymers which comprise one or more repeat units A (as defined herein) are themselves new and patentable compounds and accordingly such polymers are also provided according to the invention.

There is further provided according to the invention a method of treating a surface of an object which method comprises applying to said surface a coating composition as defined herein thereby to form on the surface (after removal of any liquid carrier) a water-erodible coating.

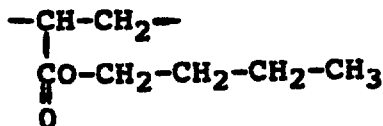
Naturally the said at least one erodible polymer of the coating composition will be dispersed or dissolved in a suitable medium, vehicle or carrier therefor in the composition; this may comprise mainly water, i.e. be aqueous-based, but can also be (and usually is) organic-based (e.g. xylene, methanol, ethanol or ethanol/water-based) or even a liquid prepolymer. Other ingredients as required may also be included in the composition. Examples of these include additional polymeric materials (optionally also water-erodible but not of course as already defined above), biocides of one sort or another (e.g. algicides, fungicides, bacteriocides) - but preferably not based on tin - to impart or enhance antifouling behaviour, catalysts and plasticisers (or other types of diluent or filler) for further controlling the hydrolysis rate (catalysts for speeding it up for example, and plasticisers for slowing it down), releasable (diffusion-controlled) hydrocarbon and silicon oils, again for further enhancing antifouling behaviour (see before), stabilisers, fillers, pigments, dyes, anti-rust agents, coalescing agents, thickeners, defoamers, and/or any other material required for any particular application. Such substances (if used) may be incorporated or formulated into the composition by any suitable technique. It is particularly envisaged that the composition will be in the form of a paint for application to the surface, and will therefore include materials commonly used in paint formulations, such as pigments and other ingredients where appropriate (extenders, stabilisers, thickeners, coalescing solvents, defoamers, surfactants, and so on).

The method of the invention is applicable to a variety of solid objects, for example, vessels, pipes and machinery of all types, e.g. stills and paper mills, having one or more surfaces that will come into contact with an aqueous medium capable of eroding the surface of the applied coating. The invention is especially applicable to the hulls of ships and boats and to other structures used in a marine environment. Moreover, the object which is treated in accordance with the method of the invention may itself be a solid coating, for example a paint coating which has been applied to a substrate for protective or decorative purposes and which itself requires protection from adhesive organisms. In some cases the composition may be part of a surface coating formulation which is to be applied to a surface so that the surface coating formulation serves as a vehicle for the composition without impairing the erodibility of the coating.

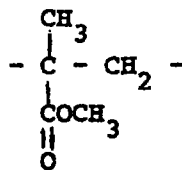
Surfaces which may be treated in accordance with the invention include the surfaces of inorganic materials such as metals, glass or silica and organic materials such as plastics articles and other polymeric materials such as the aforementioned coatings.

The most suitable technique for applying the composition to the surface depends upon the particular composition and surface involved and also upon the situation in which intestation is likely to occur. Application by brush, roller, pad, dipping, and spraying are e.g. envisaged where appropriate.

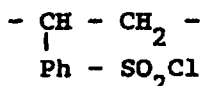
The present invention is now illustrated by the following examples. Unless otherwise specified all parts, percentages and ratios are on a weight basis, except for the proportions of monomer-derived units in polymers which are all expressed on a mole % basis. The following abbreviations are employed in the examples: n-BA: repeat unit derived n-butyl acrylate, i.e. of formula



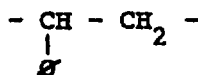
MMA : repeat unit derived from methyl methacrylate, i.e. of formula



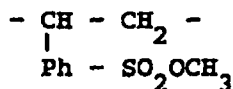
SSCl : repeat unit derived from styrene p-sulphonyl chloride, i.e. of formula



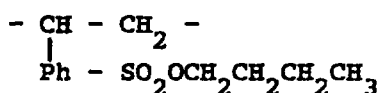
S : (-Ph- is p-phenylene)
repeat unit derived from styrene, i.e. of formula



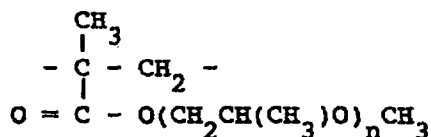
SSE (alkyl) : (ϕ is phenyl)
repeat unit derived from styrene p-sulphonate alkyl ester, with the alkyl group from the alkanol following in parenthesis, e.g. SSE (methyl) has the formula



SSE (n-butyl) has the formula



PPGMA : repeat unit of the formula



where n is 5 and 6 (mainly) (giving rise to average value for n of about 5.5).

Examples 1 to 15

Copolymers according to the invention (Examples 1 to 15) were prepared by copolymerising styrene p-sulphonyl chloride ($\text{CH}_2=\text{CH}-\text{Ph}-\text{SO}_2\text{Cl}$ where -Ph- is para phenylene) either with n-butyl acrylate and methyl methacrylate, or with n-butyl acrylate and styrene, to yield copolymers with pendant -Ph-SO₂Cl groups, followed by esterification of the sulphonyl chloride groups with various alkanols to yield the various copolymers according to the invention.

Synthesis of styrene p-sulphonyl chloride

A flask containing 300 ml dry dimethyl formamide was cooled in an ice/salt bath to 3°C. Thionyl chloride (250 ml) was added dropwise with stirring over a period of 2 hrs. Sodium styrene p-sulphonate (200 g) was added in aliquots over a further 1 hour. The reaction mixture was allowed to stand for 24 hours at room temperature. The solution was poured onto ice and extracted with toluene (1000 ml). The extract was neutralised with sodium carbonate, washed with water, dried over magnesium sulphate and the solvent removed by evaporation under vacuum at 30°C. Finally the purified styrene p-sulphonyl chloride was filtered and stored at 5°C in the dark.

The above procedure closely followed that described by Kamogawa et al (Bull Chem Soc Japan 56 762 1983).

Synthesis of copolymers with pendant sulphonyl chloride groups

a) Using n-butyl acrylate and methyl methacrylate as comonomers.

A typical polymerisation is described. Polymerisation was carried out in 4-necked reaction vessel. n-Butyl acrylate (0.8 mole) and methyl methacrylate (0.8 mole) were added with xylene (500 ml) to the flask and the vessel contents stirred for 1 hour at 68°C. Nitrogen was bled through the system to remove oxygen. After degassing, azoisobutyronitrile (AIBN) initiator (4.87 g) was added. A solution of styrene p-sulphonyl chloride (0.4 mole) and AIBN initiator (4.87 g) in xylene (90 ml) was fed into the stirred reaction vessel by means of a peristaltic pump at a rate of 2 ml per minute and polymerisation was continued for 24 hours at 68°C to form the copolymer. It was found by chemical analysis that the comonomers used reacted to give corresponding repeat units in the copolymer which were present in relative mole ratios very close the mole ratios used for the starting comonomers; this applied to all copolymers prepared. Accordingly the composition of the above described copolymer was n-BA (40 mole %)/MMA (40 mole %)/SSCl (20 mole %).

b) Using n-butyl acrylate and styrene as comonomers

Xylene (100 ml) and butyl acrylate (0.08 mole) were added to the 4-necked reaction flask and stirred for 30 minutes under nitrogen to remove dissolved oxygen. AIBN initiator, (0.164 g) was added. A mixture of styrene (0.08 mole), styrene p-sulphonyl chloride (0.04 mole), xylene (100 ml) and AIBN (0.328 g) were fed into the reaction mixture over a period of eight hours. Polymerisation was continued for 24 hours at 68°C to yield a copolymer of composition n-BA (40 mole %)/S ((40 mole %)/SSCl (20 mole %). Polymers containing 5 and 10 mole % SSCI were also prepared using this method.

Esterification of copolymers containing pendant sulphonyl chloride groups

A typical esterification is described. The solution of copolymer in xylene was used as prepared in a) or b). To a solution containing 5 g copolymer (20 mole % SSCI content), triethylamine (2×10^{-2} mole) and alkanol (2×10^{-2} mole) were added. The reaction mixture was allowed to stand for 24 hours, and filtered to remove triethylamine hydrochloride; this resulted in a clear solution in xylene of the copolymer sulphonate ester containing styrene p-sulphonate ester units (SSE units). Microanalysis of samples indicated that esterification was quantitative for all the copolymers prepared.

The following copolymer sulphonate esters according to the invention (as shown in Table I) were prepared using the processes described above.

Table 1

Example No.	Copolymer composition (units and mole % of units)	Method used for SSCL intermediate (a) or b))
1	n-BA/MMA/SSE (ethyl) 40 40 20	a)
2	n-BA/MMA/SSE (n-butyl) 40 40 20	a)
3	n-BA/MMA/SSE (n-hexyl) 40 40 20	a)
4	n-BA/S/SSE (ethyl) 40 40 20	b)
5	n-BA/S/SSE (n-propyl) 40 40 20	b)
6	n-BA/S/SSE (iso-propyl) 40 40 20	b)
7	n-BA/S/SSE (n-butyl) 40 40 20	b)
8	n-BA/S/SSE (iso-butyl) 40 40 20	b)
9	n-BA/S/SSE (tert-butyl) 40 40 20	b)
10	n-BA/S/SSE (n-hexyl) 40 40 20	b)
11	n-BA/S/SSE (cyclohexyl) 40 40 20	b)
12	n-BA/S/SSE (ethyl) 45 45 10	b)
13	n-BA/S/SSE (n-propyl) 45 45 10	b)
14	n-BA/S/SSE (n-butyl) 45 45 10	b)
15	n-BA/S/SSE (n-hexyl) 45 45 10	b)

The copolymers of Examples 1 to 15 were all in the weight average molecular weight (Mw) range of 130,000 to 240,000 (as measured by gel permeation chromatography).

It may be remarked that copolymers n-BA/MMA/SSE (alkyl) (47.5/47.5/5) have also been prepared (method a)) but not yet tested. Also, copolymers MMA/PPGMA/SSE (alkyl) (60/30/10) have been prepared (via a method similar to b)) but not yet tested.

Examples 16 to 31

Samples of the xylene solutions of the copolymers of Examples 1 to 15 were each compounded with zinc oxide (white pigment) in 65:35 copolymer solid: zinc oxide (w/w) ratios to form simple paint coating compositions (Examples 16 to 30). The hydrolytic behaviour of the copolymers of these compositions in the presence of the ZnO pigment also in the compositions (as would occur in an applied coating after drying) was estimated as follows.

Each composition was dried and pulverised using a mortar and pestle. A known weight of the desired composition was suspended in distilled water at pH 8.15 (sea water pH) at 35°C with constant agitation. The suspension was titrated with 0.01 M sodium hydroxide hourly to maintain the initial pH thereby enabling the % conversion of sulphonate ester to sulphonic acid groups to be estimated hourly. The hydrolysis results are shown in Table 2. For comparison purposes, a composition of 65 parts of a polymer mixture containing 33% of a commercially available tributyl tin methacrylate copolymer (a known self-polishing polymer) and 67% of polymethyl methacrylate with 35 parts of ZnO was prepared (Example 31) and the hydrolytic behaviour of the organo-tin-polymer therein similarly examined (see Table 2).

Table 2

Ex. No. of compn.	Ex No. of copol. used in compn.	% Conversion of ester to acid groups with time							
		1hr	2hr	3hr	4hr	5hr	6hr	7hr	8hr
16	1	0.77	1.34	1.88	2.20	2.45	2.68	2.90	nm
17	2	5.10	7.30	8.60	9.51	10.34	11.15	11.74	nm
18	3	4.41	6.48	7.72	8.65	9.14	9.72	10.11	nm
19	4	0.99	1.47	1.91	2.19	2.45	2.63	2.80	nm
20	5	0.74	1.55	2.25	2.85	3.23	3.55	nm	nm
21	6	0.22	0.60	1.19	1.73	2.30	3.06	3.80	nm
22	7	5.19	7.23	8.43	9.27	10.12	10.86	11.53	12.12
23	8	3.87	7.63	11.70	12.40	13.30	14.10	nm	nm
24	9	5.60	10.80	16.40	21.30	27.60	32.40	nm	nm
25	10	4.17	6.29	7.55	8.44	9.03	9.68	10.04	10.52
26	11	3.07	4.99	6.31	7.91	8.36	8.78	nm	nm
27	12	0.35	0.65	0.90	1.11	1.31	1.47	1.59	nm
28	13	0.35	0.65	0.92	1.19	1.39	1.58	1.75	nm
29	14	0.55	1.22	1.88	2.30	2.78	3.19	nm	nm
30	15	0.37	0.95	1.52	1.91	2.45	2.65	nm	nm
31	-	0.47	0.78	0.99	1.14	1.30	1.41	1.55	1.68

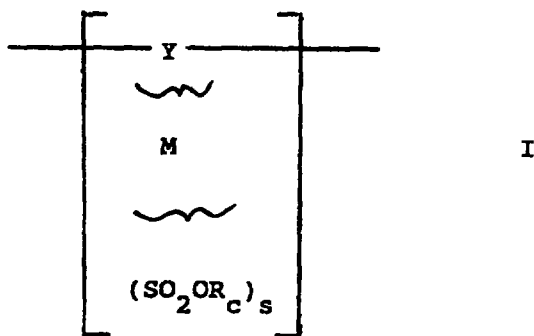
nm = not measured

It will be noted from the results in Table 2 that, as would be expected, the copolymers having 10 mole % of SSE units hydrolysed more slowly than those with copolymers containing 20 mole % of SSE, other things being equal (compare Example pairs 19, 27; 20, 28; 22, 29; and 25, 30). Also, perhaps surprisingly, the copolymers with units of the longer chain SSE alkyl esters used - SSE (n-butyl), SSE (iso-butyl), SSE-(tert-butyl), SSE (n-hexyl), SSE (cyclohexyl) - hydrolysed faster than the copolymers with the shorter chain SSE alkyl esters - SSE (ethyl), SSE (n-propyl), SSE (iso-propyl) (compare Examples 17, 18, 22, 23, 24, 25, 26).

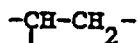
against Examples 16, 19, 20, 21, all with 20 mole % SSE units). This effect clearly allows a useful degree of control over the rate of hydrolysis in a coating to be achieved by an appropriate choice of alkyl ester. It will be noted that the known self-polishing tin-containing copolymer in Example 31 hydrolysed at about the same rate as the copolymers used for Examples 27 and 28 containing units of SSE (ethyl) and SSE (n-propyl) at a level of 10 mole % (all other copolymers hydrolysing faster to a smaller or larger degree). It was also noted that, initially, the polymer and pigment particles were tightly bound together providing a granular solid phase suspended in a clear aqueous phase but that as hydrolysis proceeded the aqueous phase became increasingly opaque (milky white) due to the release of ZnO associated with the hydrolysed polymer. Visually, this increase in opaqueness appeared to follow the rate of hydrolysis, indicating that coatings containing the copolymers would be usefully erodible.

Claims

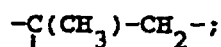
1. Coating composition suitable for treating a surface so as to provide a water-erodible coating thereon, which composition comprises at least one erodible polymer comprising 3 to 40 mole % of one or more repeat units A each comprising at least one hydrolysable sulphonate ester group pendant to the main chain backbone of the polymer, wherein said repeat unit A has the formula:



wherein Y, which in the repeat units A of formula I may be the same or different, is a group in the main chain backbone selected from



and



s is an integer of 1 or more corresponding to the number of SO_2OR_c groups in repeat unit A of formula I;

R_c , which in the same repeat unit A of formula I (when s is 2 or more) or in different repeat units A of formula I may be the same or different, is a group selected from one or more of alkyl (including primary, secondary and tertiary alkyl and cycloalkyl), aryl, alkaryl, aralkyl, alkenoxyalkyl and poly-(alkenoxy)alkyl groups;

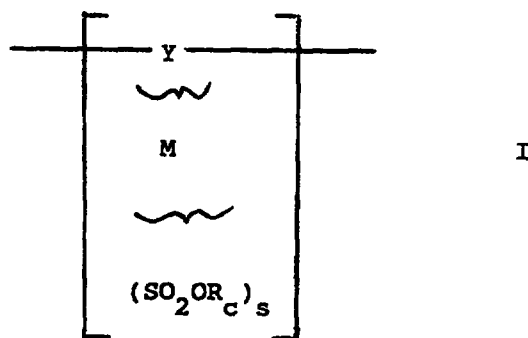
and wherein each SO_2OR_c group is joined via an intermediary M to the group Y, M being a direct link or a group selected from -(alkylene)-, -CO-O-(alkylene)-, -CO-NH-(alkylene)-, -NH-CO-(alkylene)-, -(arylene)-, -(alkylene)-(arylene)-, -(alkylene)-O-(alkylene)-, -(alkylene)-O-(arylene)-, -(arylene)-O-(arylene)-, -(arylene)-O-(alkylene)-, -alkylenoxy-, and -polyalkylenoxy-groups.

2. Coating composition according to claim 1 wherein M is selected from one or more of o, m or p-phenylene.

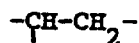
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Claims

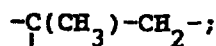
1. Coating composition suitable for treating a surface so as to provide a water-erodible coating thereon, which composition comprises at least one erodible polymer comprising 3 to 40 mole % of one or more repeat units A each comprising at least one hydrolysable sulphonate ester group pendant to the main chain backbone of the polymer, wherein said repeat unit A has the formula:



wherein Y, which in the repeat units A of formula I may be the same or different, is a group in the main chain backbone selected from



and



s is an integer of 1 or more corresponding to the number of SO_2OR_c groups in repeat unit A of formula I;

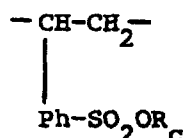
R_c , which in the same repeat unit A of formula I (when s is 2 or more) or in different repeat units A of formula I may be the same or different, is a group selected from one or more of alkyl (including primary, secondary and tertiary alkyl and cycloalkyl), aryl, alkaryl, aralkyl, alkenoxyalkyl and poly-(alkenoxo)alkyl groups;

and wherein each SO_2OR_c group is joined via an intermediary M to the group Y, M being a direct link or a group selected from -(alkylene)-, -CO-O-(alkylene)-, -CO-NH-(alkylene)-, -NH-CO-(alkylene)-, -(arylene)-, -(alkylene)-(arylene)-, -(alkylene)-O-(alkylene)-, -(alkylene)-O-(arylene)-, -(arylene)-O-(arylene)-, -(arylene)-O-(alkylene)-, -alkylenoxy-, and -polyalkylenoxy-groups.

2. Coating composition according to claim 1 wherein M is selected from one or more of o, m or p-phenylene.

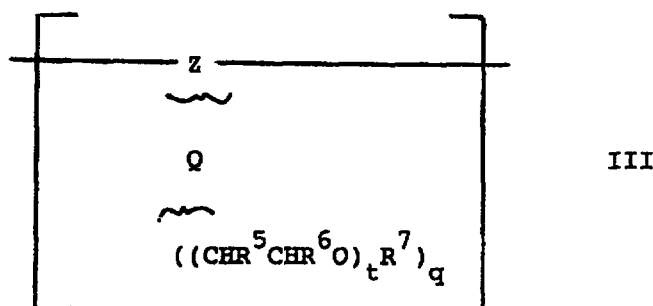


3. Coating composition according to either claim 1 or claim wherein s is 1.
4. Coating composition according to any one of the preceding claims wherein R_c is selected from one or more of alkyl (having 1 to 20 carbon atoms), phenyl and benzyl.
5. Coating composition according to any one of the preceding claims wherein repeat unit A has the formula:



where -Ph- is p-phenylene.

6. Coating composition according to any one of the preceding claims wherein said erodible polymer additionally comprises one or more repeat units C being repeat units containing at least one alkylene oxide or poly(alkylene oxide) group and not containing a sulphonate ester or sulphate ester group, wherein said repeat unit C has the formula:



wherein t is an integer of from 1 to 200;

q is an integer of from 1 to 4;

Z, which in the repeat units C of formula III may be the same or different, is a hydrocarbyl residue or a substituted derivative thereof;

R^5 which is the same repeat unit C of formula III (when t or q is two or more) or in different repeat units C of formula III may be the same or different, is hydrogen or methyl;

R^6 which in the same repeat unit C of formula III (when t or q is 2 or more) or in different repeat units C of formula III may be the same or different, is hydrogen or methyl;

except that R^5 and R^6 in a single unit $(\text{CHR}^5\text{CHR}^6\text{O})$ cannot both be methyl;

R^7 which in the same repeat unit C of formula III (when q is 2 or more) or in different repeat units C of formula III may be the same or different, is hydrogen, an alkyl group, or an acyl group;

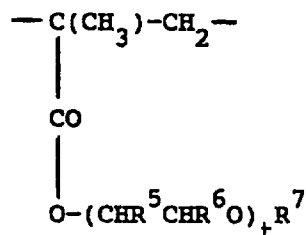
and wherein each $(\text{CHR}^5\text{CHR}^6\text{O})_t$ group is joined via an intermediary or intermediaries Q to the hydrocarbyl residue Z, and in cases where q is 2 to 4 may be joined by Q to the same or different carbon atoms of Z;

and wherein Q represents one or more intermediaries and wherein Q may be the same or different in the repeat units C of formula III and is selected from one or more direct links and one or more atoms or groups of atoms providing a chain of one or more atoms for linking a $(\text{CHR}^5\text{CHR}^6\text{O})_t$ group with Z, except that more than two $(\text{CHR}^5\text{CHR}^6\text{O})_t$ groups cannot be directly linked to the same carbon atom in Z if that carbon atom forms part of the main chain polymer backbone.

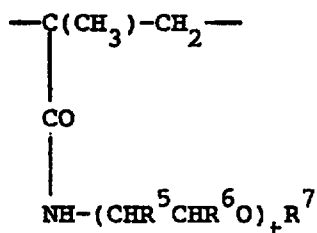
7. Coating composition according to claim 6 wherein q is 1 or 2.
8. Coating composition according to either claim 6 or claim 7 wherein t is 1 to 60.



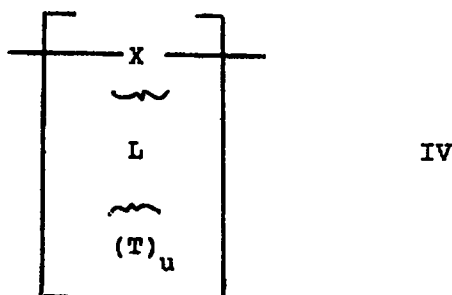
9. Coating composition according to any one of claims 6 to 8 wherein a repeat unit C has the formula:



or



10. Coating composition according to any one of the preceding claims wherein said erodible polymer comprises 0 to 50 mole % of repeat units C.
11. Coating composition according to claim 10 wherein said erodible polymer comprises 0 to 40 mole % of repeat units C.
12. Coating composition according to any one of the preceding claims wherein said erodible polymer additionally comprises one or more repeat units D being repeat units which contain at least one acidic and/or basic group, wherein repeat unit D has the formula:



wherein X, which in the repeat units D of formula IV may be the same or different, is a hydrocarbyl residue or a substituted derivative thereof;

u is an integer of 1 to 4;

T, which in the repeat units D of formula IV may be the same or different, is a group bearing an acid or basic substituent (other than a substituent derivable from sulphonate or sulphate ester hydrolysis);

and wherein each T group is joined via an intermediary or intermediaries L to the hydrocarbyl residue X, and in cases where u is 2 to 4 may be joined by L to the same or different carbon atoms of X; and

wherein L represents one or more intermediaries and wherein L may be the same or different in the repeat units D of formula IV and is selected from one or more direct links and one or more atoms or groups of atoms providing a chain of one or more atoms for linking a T group with X, except that more than two T groups cannot be directly linked to the same carbon atom in X if that carbon atom forms



part of the main chain polymer backbone.

13. Coating composition according any one of the preceding claims wherein said erodible polymer comprises 0 to 30% of repeat units D.

14. Coating composition according to any one of the preceding claims wherein said erodible polymer additionally comprises one or more repeat units E, being repeat units other than those containing sulphonate ester or sulphate ester groups or having the structure of repeat units C or D.

15. Coating composition according to claim 14 wherein said erodible polymer comprises 5 to 97 mole % of repeat units E.

16. Coating composition according to either claim 14 or claim 15 wherein the repeat units E are derived from one or more monomers selected from esters and amides of olefinically unsaturated carboxylic acids, alpha aryl-substituted monoolefins, vinyl esters, vinyl halides, vinylidene halides and olefinically unsaturated nitriles.

17. Coating composition according to claim 16 wherein the repeat units E are derived from one or more monomers selected from methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, acrylamide, methacrylamide, styrene, alpha-methyl styrene, vinyl chloride, vinylidene chloride, acrylonitrile and methacrylonitrile.

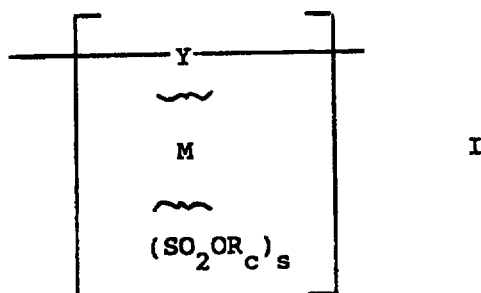
18. Coating composition according to any one of the preceding claims wherein said erodible polymer comprises 3 to 40 mole % of one or more repeat units A, 0 to 40% mole % of one or more repeat units C, 0 to 20 mole % of one or more repeat units D, and 5 to 97 mole % of one or more repeat units E.

19. Coating composition according to any one of the preceding claims wherein said erodible polymer has a weight average molecular weight (M_w) in the range 50,000 to 300,000.

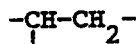
20. Coating composition according to any one of the preceding claims in the form of an aqueous-or organic liquid-based paint composition and comprising at least one pigment.

21. Coating composition according to any one of the preceding claims which composition includes at least one biocide.

22. Water erodible polymer which comprises 3 to 40 mole % of one or more repeat units A each comprising at least one hydrolysable sulphonate ester group pendant to the main chain backbone of the polymer, wherein said repeat unit A has the formula:

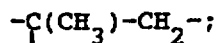


wherein Y, which in the repeat units A of formula I may be the same or different, is a group in the main chain backbone selected from



and





s is an integer of 1 or more corresponding to the number of SO_2OR_c groups in repeat unit A of formula I;

R_c , which in the same repeat unit A of formula I (when s is 2 or more) or in different repeat units A of formula I may be the same or different, is a group selected from one or more of alkyl (including primary, secondary and tertiary alkyl and cycloalkyl), aryl, alkaryl, aralkyl, alkenoxyalkyl and poly-(alkenoxy)alkyl groups;

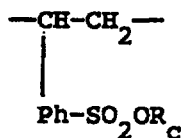
and wherein each SO_2OR_c group is joined via an intermediary M to the group Y, M being a direct link or a group selected from -(alkylene)-, -CO-O-(alkylene)-, -CO-NH-(alkylene)-, -NH-CO-(alkylene)-, -(arylene)-, -(alkylene)-(arylene)-, -(alkylene)-O-(alkylene)-, -(alkylene)-O-(arylene)-, -(arylene)-O-(arylene), -(arylene)-O-(alkylene)-, -alkylenoxy-, and -polyalkylenoxy-groups.

23. Polymer according to claim 22 wherein M is selected from one or more of o, m and p-phenylene.

24. Polymer according to either claim 22 or claim 23 wherein s is 1.

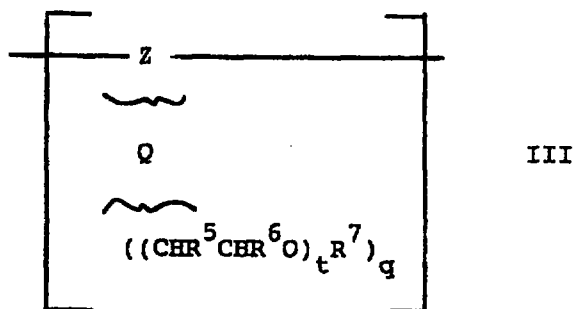
25. Polymer according to any one of claims 22 to 24 wherein R_c is selected from one or more of alkyl (having 1 to 20 carbon atoms), phenyl and benzyl.

26. Polymer according to any one of claims 22 to 25 wherein repeat unit A has the formula:



where -Ph- is p-phenylene.

27. Polymer according to any one of claims 22 to 26 wherein said polymer additionally comprises one or more repeat units C, being repeat units comprising at least one alkylene oxide or poly(alkylene oxide) group and not containing a sulphonate ester or sulphate ester group wherein repeat unit C has the formula:



wherein t is an integer of from 1 to 200;

q is an integer of from 1 to 4;

Z, which in the repeat units C of formula III may be the same or different, is a hydrocarbyl residue or a substituted derivative thereof;

R^5 , which in the same repeat unit C of formula III (when t or q is two or more) or in different repeat units C of formula III may be the same or different, is hydrogen or methyl;



R^6 , which in the same repeat unit C of formula III (when t or q is 2 or more) or in different repeat units C of formula III may be the same or different, is hydrogen or methyl;

except that R^5 and R^6 in a single unit (CHR^5CHR^6O) cannot both be methyl;

R^7 , which in the same repeat unit C of formula III (when q is 2 or more) or in different repeat units C of formula III may be the same or different, is hydrogen, or an alkyl group, or an acyl group;

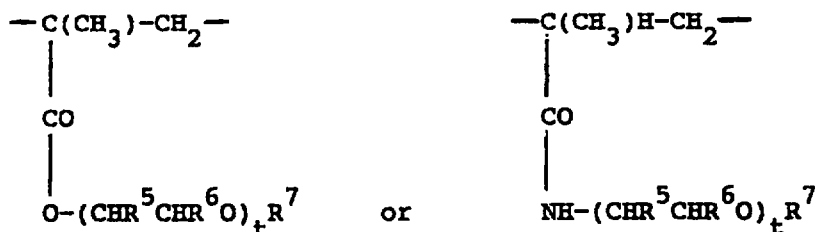
and wherein each $(CHR^5CHR^6O)_t$ group is joined via an intermediary or intermediaries Q to the hydrocarbonyl residue Z, and in cases where Q is 2 to 4 may be joined by Q to the same or different carbon atoms of Z;

and wherein Q represents one or more intermediaries and wherein Q may be the same or different in the repeat units C of formula III and is selected from one or more direct links and one or more atoms or groups of atoms providing a chain of one or more atoms for linking a $(CHR^5CHR^6O)_t$ group with Z, except that more than two $(CHR^5CHR^6O)_t$ groups cannot be directly linked to the same carbon atom in Z if that carbon atom forms part of the main chain polymer backbone.

28. Polymer according to claim 27 wherein q is 1 or 2.

29. Polymer according to either claim 27 or claim 28 wherein t is 1 to 60.

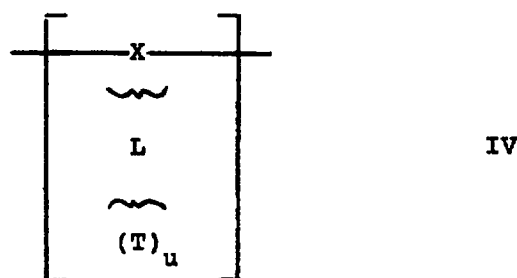
30. Polymer according to any one of claims 27 to 29 wherein repeat unit C has the formula:



31. Polymer according to any one of claims 22 to 30 wherein the erodible polymer comprises 0 to 50 mole % of repeat units C.

32. Polymer according to claim 31 wherein said polymer comprises 0 to 40 mole % of repeat units C.

33. Polymer according to any one of claims 22 to 32 wherein said polymer additionally comprises one or more repeat units D being repeat units which contain at least one acidic and/or basic group, wherein repeat unit D has the formula:



wherein X, which in the repeat units D of formula IV may be the same or different, is a hydrocarbonyl residue or a substituted derivative thereof;

u is an integer of 1 to 4;

T, which in the repeat units D of formula IV may be the same or different, is a group bearing an acid or basic substituent (other than a substituent derivable from sulphonate or sulphate ester hydrolysis);

and wherein each T group is joined via an intermediary or intermediaries L to the hydrocarbonyl residue X, and in cases where u is 2 to 4 may be joined by L to the same or different carbon atoms of X; and



wherein L represents one or more intermediaries and wherein L may be the same or different in the repeat units D of formula IV and is selected from one or more direct links and one or more atoms or groups of atoms providing a chain of one or more atoms for linking a T group with X, except that more than two T groups cannot be directly linked to the same carbon atom in X if that carbon atom forms part of the main chain polymer backbone.

34. Polymer according to any one of claims 22 to 33 wherein said polymer comprises 0 to 30 mole % of repeat units D.

35. Polymer according to any one of claims 22 to 34 wherein said polymer comprises one or more repeat units E, being repeat units other than those containing sulphonate ester or sulphate ester groups or having the structures of repeat units C or D.

36. Polymer according to claim 35 wherein said polymer comprises 5 to 97 mole % of repeat units E.

37. Polymer according to either claim 35 or claim 36 wherein the repeat units E are derived from one or more monomers selected from esters and amides of olefinically unsaturated carboxylic acids, alpha aryl-substituted monoolefins, vinyl esters, vinyl halides, vinylidene halides, and olefinically unsaturated nitriles.

38. Polymer according to claim 37 wherein the repeat units E are derived from one or more monomers selected from methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, acrylamide, methacrylamide, styrene, alpha-methyl styrene vinyl chloride, vinylidene chloride, acrylonitrile and methacrylonitrile.

39. Polymer according to any one of claims 22 to 38 wherein said polymer comprises 3 to 40 mole % of one or more repeat units A, 0 to 40 mole % of one or more repeat units C, 0 to 20% mole % of one or more repeat units D, and 5 to 97 mole % of one or more repeat units E.

40. Polymer according to any one of claims 22 to 39 wherein said polymer has a weight average molecular weight (M_w) in the range 50,000 to 300,000.

41. Method of treating a surface which method comprises applying to the surface a water-erodible coating composition according to any one of claims 1 to 21 thereby to form on the surface a water-erodible coating.

42. Process for the production of a water-erodible polymer, which process comprises polymerising monomers comprising at least one monomer of formula $\text{CH}_2 = \text{CHMSO}_2\text{G}$, said at least one monomer being used in an amount to provide 3 to 40 mole % of repeat units derived therefrom in the final polymer, wherein:

G is a group readily convertible by an esterification reaction to an $-\text{OR}_c$ group after polymerisation;

R_c is a group selected from alkyl (including primary, secondary and tertiary alkyl and cycloalkyl), aryl, alkaryl, aralkyl, alkenoxyalkyl and poly(alkenoxo)alkyl groups;

M is a direct link or a group selected from $-(\text{alkylene})-$, $-\text{CO}-\text{O}-(\text{alkylene})-$, $-\text{CO}-\text{NH}-(\text{alkylene})-$, $-\text{NH}-\text{CO}-(\text{alkylene})-$, $-(\text{arylene})-$, $-(\text{alkylene})-(\text{arylene})-$, $-(\text{alkylene})-\text{O}-(\text{alkylene})-$, $-(\text{alkylene})-\text{O}-(\text{arylene})-$, $-(\text{arylene})-\text{O}-(\text{arylene})-$, $-(\text{arylene})-\text{O}-(\text{alkylene})-$, $-\text{alkylenoxy}-$, and $-\text{polyalkylenoxy}-$ groups;

and thereafter carrying out an esterification reaction using a compound of formula R_cOH .

43. Process according to claim 42 wherein G is Cl.

44. Process according to either claim 42 or claim 43 wherein M is para phenylene.

45. Process according to any one of claims 42 to 44 wherein R_c is alkyl of 1 to 20 carbon atoms.

46. Process according to claim 45 wherein R_c is methyl.

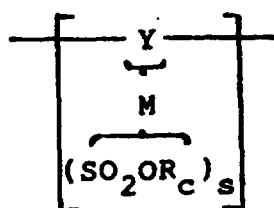


47. Process according to any one of claims 42 to 46 wherein the esterification is performed in the presence of triethylamine.

48. The water-erodible polymer formed by a process according to any one of claims 42 to 47.

Revendications

1. Composition de revêtement convenant pour traiter une surface aux fins de former sur celle-ci un revêtement érodable par l'eau, laquelle composition comprend au moins un polymère érodable comprenant 3 à 40 moles % d'une ou plusieurs unités récurrentes A comprenant chacune au moins un radical ester sulfonique hydrolysable pendant sur la chaîne principale du squelette du polymère, où l'unité récurrente de formule A est de formule :



I

où Y, qui, dans les unités récurrentes A de formule I, peut être identique ou différent, est un radical dans la chaîne principale du squelette choisie entre $>\text{CH}-\text{CH}_2-$ et $>\text{C}(\text{CH}_3)-\text{CH}_2-$;

s est un entier de 1 ou davantage correspondant au nombre de radicaux SO_2OR_c dans l'unité récurrente A de formule I;

R_c , qui, dans la même unité récurrente A de formule I (lorsque s est 2 ou davantage) ou dans des unités récurrentes A de formule I différentes peut être identique ou différent, est un radical choisi parmi un ou plusieurs d'entre des radicaux alcoyle (notamment alcoyle primaire, secondaire et tertiaire et cycloalcoyl), aryle, alcaryle, aralcoyle, alcénoxyalcoyle et poly(alcénoxy)alcoyle;

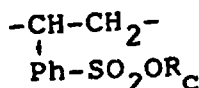
et où chaque radical SO_2OR_c est uni par un intermédiaire M au radical Y, M étant un lien direct ou un radical choisi parmi les radicaux $-(\text{alcoylène})-$, $-\text{CO}-\text{O}-(\text{alcoylène})-$, $-\text{CO}-\text{NH}-(\text{alcoylène})-$, $-\text{NH}-\text{CO}-(\text{alcoylène})-$, $-(\text{arylène})-$, $-(\text{alcoylène})-(\text{arylène})-$, $-(\text{alcoylène})-\text{O}-(\text{alcoylène})-$, $-(\text{alcoylène})-\text{O}-(\text{arylène})-$, $-(\text{arylène})-\text{O}-(\text{arylène})-$, $-(\text{arylène})-\text{O}-(\text{alcoylène})-$, $-\text{alcoylénoxy}-$ et $-\text{polyalcoylénoxy}-$.

2. Composition de revêtement suivant la revendication 1, dans laquelle M est choisi parmi un ou plusieurs d'entre o-, m- et p-phénylène.

3. Composition de revêtement suivant la revendication 1 ou 2, dans laquelle s est 1.

4. Composition de revêtement suivant l'une quelconque des revendications précédentes, dans laquelle R_c est choisi parmi un ou plusieurs d'entre alcoyle (comptant 1 à 20 atomes de carbone), phényle et benzyle.

5. Composition de revêtement suivant l'une quelconque des revendications précédentes, dans laquelle l'unité récurrente A est de formule :

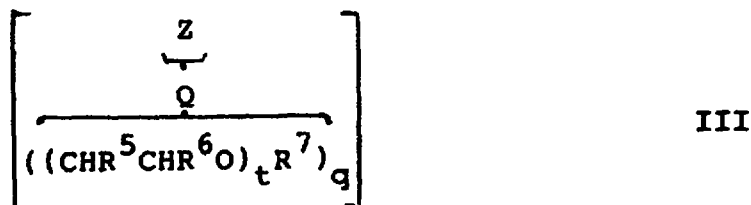


où -Ph- est p-phénylène.

6. Composition de revêtement suivant l'une quelconque des revendications précédentes, dans laquelle le polymère érodable comprend, en outre, une ou plusieurs unités récurrentes C qui sont des unités



récurrentes contenant au moins un radical oxyde d'alcoylène ou poly(oxyde d'alcoylène) et ne contenant pas un radical ester sulfonique ou ester sulfurique, où l'unité récurrente C est de formule :



où t est un entier de 1 à 200;

q est un entier de 1 à 4;

Z, qui, dans les mêmes unités récurrentes C de formule III peut être identique ou différent, est un résidu hydrocarbyle ou un dérivé substitué de celui-ci;

R⁵, qui, dans la même unité récurrente C de formule III (lorsque t ou q est 2 ou davantage) ou dans des unités récurrentes C de formule III différentes peut être identique ou différent, est hydrogène ou méthyle;

R⁶, qui, dans la même unité récurrente C de formule III (lorsque t ou q est 2 ou davantage) ou dans des unités récurrentes C de formule III différentes peut être identique ou différent, est hydrogène ou méthyle;

sauf que R⁵ et R⁶ dans une seule unité (CHR⁵CHR⁶O) ne peuvent être tous deux méthyle;

R⁷, qui, dans la même unité récurrente C de formule III (lorsque q est 2 ou davantage) ou dans des unités récurrentes C de formule III différentes peut être identique ou différent, est hydrogène, un radical alcoyle ou un radical acyle;

et où chaque radical (CHR⁵CHR⁶O)_t est uni par un intermédiaire ou des intermédiaires Q au résidu hydrocarbyle Z, et dans les cas où q est 2 à 4 peut être uni par Q au même atome de carbone ou à des atomes de carbone différents de Z;

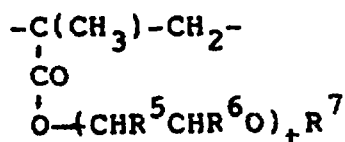
et où Q représente un ou plusieurs intermédiaires et où Q peut être identique ou différent dans les unités récurrentes C de formule III et est choisi parmi un ou plusieurs liens directs et un ou plusieurs atomes ou groupes d'atomes apportant une chaîne d'un ou plusieurs atomes pour unir un radical (CHR⁵CHR⁶O)_t à Z,

sauf que plus de deux radicaux (CHR⁵CHR⁶O)_t ne peuvent être unis directement au même atome de carbone dans Z si cet atome de carbone fait partie de la chaîne principale du squelette du polymère.

7. Composition de revêtement suivant la revendication 6, dans laquelle q est 1 ou 2.

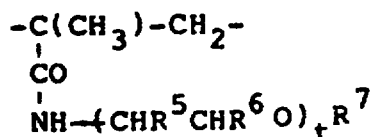
8. Composition de revêtement suivant la revendication 6 ou 7, dans laquelle t est 1 à 60.

9. Composition de revêtement suivant l'une quelconque des revendications 6 à 8, dans laquelle une unité récurrente C est de formule :



ou

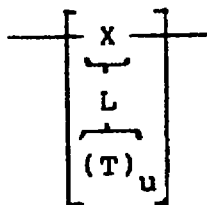




10. Composition de revêtement suivant l'une quelconque des revendications précédentes, dans laquelle le polymère érodable comprend 0 à 50 moles % d'unités récurrentes C.

11. Composition de revêtement suivant la revendication 10, dans laquelle le polymère érodable comprend 0 à 40 moles % d'unités récurrentes C.

12. Composition de revêtement suivant l'une quelconque des revendications précédentes, dans laquelle le polymère érodable comprend, en outre, une ou plusieurs unités récurrentes D qui sont des unités récurrentes qui contiennent au moins un radical acide et/ou basique, où l'unité récurrente D est de formule :



IV

où X, qui, dans l'unité récurrente D de formule IV, peut être identique ou différent, est un résidu hydrocarbyle ou un dérivé substitué de celui-ci;

u est un entier de 1 à 4;

T, qui, dans les unités récurrentes D de formule IV peut être identique ou différent, est un radical portant un substituant acide ou basique (autre qu'un substituant pouvant dériver de l'hydrolyse d'un ester sulfonique ou sulfurique);

et où chaque radical T est uni par un intermédiaire ou des intermédiaires L au résidu hydrocarbyle X et, dans les cas où u est 2 à 4, peut être uni par L au même atome de carbone ou à des atomes de carbone différents de X; et

où L représente un ou plusieurs intermédiaires et L peut être identique ou différent dans les unités récurrentes D de formule IV et est choisi parmi un ou plusieurs liens directs et un ou plusieurs atomes ou groupes d'atomes apportant une chaîne d'un ou plusieurs atomes pour unir un radical T à X, sauf que plus de deux radicaux T ne peuvent être unis directement au même atome de carbone dans X si cet atome de carbone fait partie de la chaîne principale du squelette de polymère.

13. Composition de revêtement suivant l'une quelconque des revendications précédentes, dans laquelle le polymère érodable comprend 0 à 30 moles % d'unités récurrentes D.

14. Composition de revêtement suivant l'une quelconque des revendications précédentes, dans laquelle le polymère érodable comprend, en outre, une ou plusieurs unités récurrentes E qui sont des unités récurrentes autres que celles contenant des radicaux ester sulfonique ou ester sulfurique ou ayant la structure des unités récurrentes C ou D.

15. Composition de revêtement suivant la revendication 14, dans laquelle le polymère érodable comprend 5 à 97 moles % d'unités récurrentes E.

16. Composition de revêtement suivant la revendication 14 ou 15, dans laquelle les unités récurrentes E dérivent d'un ou plusieurs monomères choisis parmi les esters et amides d'acides carboxyliques oléfiniquement insaturés, les monooléfines alpha aryl-substituées, les esters vinyliques, les halogénures



de vinyle, les halogénures de vinylidène et les nitriles oléfiniquement insaturés.

17. Composition de revêtement suivant la revendication 16, dans laquelle les unités récurrentes E dérivent d'un ou plusieurs monomères choisis parmi l'acrylate de méthyle, le méthacrylate de méthyle, l'acrylate d'éthyle, le méthacrylate d'éthyle, l'acrylate de n-butyle, l'acrylamide, le méthacrylamide, le styrène, l'alpha-méthylstyrène, le chlorure de vinyle, le chlorure de vinylidène, l'acrylonitrile et le méthacrylonitrile.

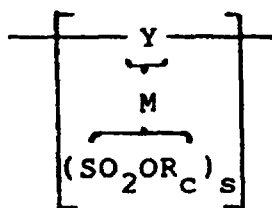
18. Composition de revêtement suivant l'une quelconque des revendications précédentes, dans laquelle le polymère érodable comprend 3 à 40 moles % d'une ou plusieurs unités récurrentes A, 0 à 40 moles % d'une ou plusieurs unités récurrentes C, 0 à 20 moles % d'une ou plusieurs unités récurrentes D et 5 à 97 moles % d'une ou plusieurs unités récurrentes E.

19. Composition de revêtement suivant l'une quelconque des revendications précédentes, dans laquelle le polymère érodable a un poids moléculaire moyen en masse (M_m) de l'intervalle de 50.000 à 300.000.

20. Composition de revêtement suivant l'une quelconque des revendications précédentes, sous la forme d'une composition de peinture à base de liquide aqueux ou organique et comprenant au moins un pigment.

21. Composition de revêtement suivant l'une quelconque des revendications précédentes, laquelle composition comprend au moins un biocide.

22. Polymère érodable par l'eau qui comprend 3 à 40 moles % d'une ou plusieurs unités récurrentes A comprenant chacune au moins un radical ester sulfonique hydrolysable pendant sur la chaîne principale du squelette du polymère, où l'unité récurrente de formule A est de formule :



I

où Y, qui, dans les unités récurrentes A de formule I, peut être identique ou différent, est un radical dans la chaîne principale du squelette choisie entre $>\text{CH}-\text{CH}_2-$ et $>\text{C}(\text{CH}_3)-\text{CH}_2-$;

s est un entier de 1 ou davantage correspondant au nombre de radicaux SO_2OR_c dans l'unité récurrente A de formule I;

R_c , qui, dans la même unité récurrente A de formule I (lorsque s est 2 ou davantage) ou dans des unités récurrentes A de formule I différentes peut être identique ou différent, est un radical choisi parmi un ou plusieurs d'entre des radicaux alcoyle (notamment alcoyle primaire, secondaire et tertiaire et cycloalcoyle), aryle, alcaryle, aralcoyle, alcénoxyalcoyle et poly(alcénoxy)alcoyle;

et où chaque radical SO_2OR_c est uni par un intermédiaire M au radical Y, M étant un lien direct ou un radical choisi parmi les radicaux $-(\text{alcoylène})-$, $-\text{CO}-\text{O}-(\text{alcoylène})-$, $-\text{CO}-\text{NH}-(\text{alcoylène})-$, $-\text{NH}-\text{CO}-(\text{alcoylène})-$, $-(\text{arylène})-$, $-(\text{alcoylène})-(\text{arylène})-$, $-(\text{alcoylène})-\text{O}-(\text{alcoylène})-$, $-(\text{alcoylène})-\text{O}-(\text{arylène})-$, $-(\text{arylène})-\text{O}-(\text{arylène})-$, $-(\text{arylène})-\text{O}-(\text{alcoylène})-$, $-\text{alcoylénoxy}-$ et $-\text{polyalcoylénoxy}-$.

23. Polymère suivant la revendication 22, dans lequel M est choisi parmi un ou plusieurs d'entre o-, m- et p-phénylène.

24. Polymère suivant la revendication 22 ou 23, dans lequel s est 1.

25. Polymère suivant l'une quelconque des revendications 22 à 24, dans lequel R_c est choisi parmi un ou plusieurs d'entre alcoyle (comptant 1 à 20 atomes de carbone), phényle et benzyle.

26. Polymère suivant l'une quelconque des revendications 22 à 25, dans lequel l'unité récurrente A est de

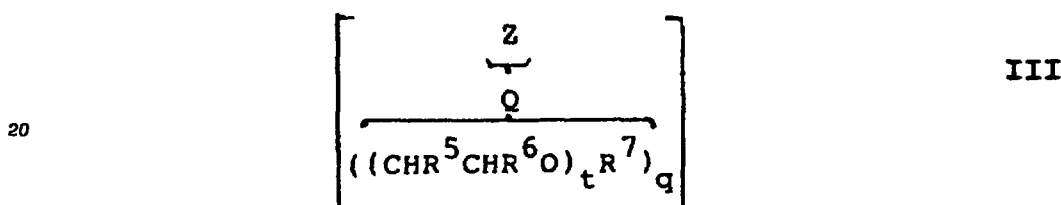


formule :



où -Ph- est p-phénylène.

27. Polymère suivant l'une quelconque des revendications 22 à 26, dans lequel le polymère comprend, en outre, une ou plusieurs unités récurrentes C qui sont des unités récurrentes contenant au moins un radical oxyde d'alcoylène ou poly(oxyde d'alcoylène) et ne contenant pas un radical ester sulfonique ou ester sulfurique, où l'unité récurrente C est de formule :



où t est un entier de 1 à 200;

q est un entier de 1 à 4;

Z, qui, dans les mêmes unités récurrentes C de formule III peut être identique ou différent, est un résidu hydrocarbyle ou un dérivé substitué de celui-ci;

R⁵, qui, dans la même unité récurrente C de formule III (lorsque t ou q est 2 ou davantage) ou dans des unités récurrentes C de formule III différentes peut être identique ou différent, est hydrogène ou méthyle;

R⁶, qui, dans la même unité récurrente C de formule III (lorsque t ou q est 2 ou davantage) ou dans des unités récurrentes C de formule III différentes peut être identique ou différent, est hydrogène ou méthyle;

sauf que R⁵ et R⁶ dans une seule unité (CHR⁵CHR⁶O) ne peuvent être tous deux méthyle;

R⁷, qui, dans la même unité récurrente C de formule III (lorsque q est 2 ou davantage) ou dans des unités récurrentes C de formule III différentes peut être identique ou différent, est hydrogène, un radical alcoyle ou un radical acyle;

et où chaque radical (CHR⁵CHR⁶O)_t est uni par un intermédiaire ou des intermédiaires Q au résidu hydrocarbyle Z, et dans les cas où q est 2 à 4 peut être uni par Q au même atome de carbone ou à des atomes de carbone différents de Z;

et où Q représente un ou plusieurs intermédiaires et où Q peut être identique ou différent dans les unités récurrentes C de formule III et est choisi parmi un ou plusieurs liens directs et un ou plusieurs atomes ou groupes d'atomes apportant une chaîne d'un ou plusieurs atomes pour unir un radical (CHR⁵CHR⁶O)_t à Z,

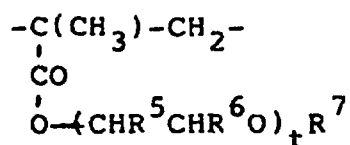
sauf que plus de deux radicaux (CHR⁵CHR⁶O)_t ne peuvent être unis directement au même atome de carbone dans Z si cet atome de carbone fait partie de la chaîne principale du squelette du polymère.

28. Polymère suivant la revendication 27, dans lequel q est 1 ou 2.

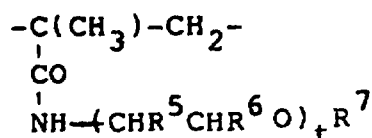
29. Polymère suivant la revendication 27 ou 28, dans lequel t est 1 à 60.

30. Polymère suivant l'une quelconque des revendications 27 à 29, dans lequel l'unité récurrente C est de formule :





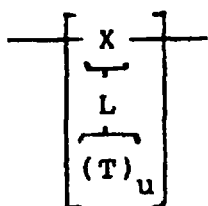
ou



31. Polymère suivant l'une quelconque des revendications 22 à 30, dans lequel le polymère érodable comprend 0 à 50 moles % d'unités récurrentes C.

32. Polymère suivant la revendication 31, dans lequel le polymère comprend 0 à 40 moles % d'unités récurrentes C.

33. Polymère suivant l'une quelconque des revendications 22 à 32, dans lequel le polymère comprend, en outre, une ou plusieurs unités récurrentes D qui sont des unités récurrentes qui contiennent au moins un radical acide et/ou basique, où l'unité récurrente D est de formule :



IV

où X, qui, dans l'unité récurrente D de formule IV, peut être identique ou différent, est un résidu hydrocarbyle ou un dérivé substitué de celui-ci;

u est un entier de 1 à 4;

T, qui, dans les unités récurrentes D de formule IV peut être identique ou différent, est un radical portant un substituant acide ou basique (autre qu'un substituant pouvant dériver de l'hydrolyse d'un ester sulfonique ou sulfurique);

et où chaque radical T est uni par un intermédiaire ou des intermédiaires L au résidu hydrocarbyle X et, dans les cas où u est 2 à 4, peut être uni par L au même atome de carbone ou à des atomes de carbone différents de X; et

où L représente un ou plusieurs intermédiaires et L peut être identique ou différent dans les unités récurrentes D de formule IV et est choisi parmi un ou plusieurs liens directs et un ou plusieurs atomes ou groupes d'atomes apportant une chaîne d'un ou plusieurs atomes pour unir un radical T à X, sauf que plus de deux radicaux T ne peuvent être unis directement au même atome de carbone dans X si cet atome de carbone fait partie de la chaîne principale du squelette de polymère.

34. Polymère suivant l'une quelconque des revendications 22 à 33, dans lequel le polymère comprend 0 à 30 moles % d'unités récurrentes D.

35. Polymère suivant l'une quelconque des revendications 22 à 34, dans lequel le polymère comprend, en outre, une ou plusieurs unités récurrentes E qui sont des unités récurrentes autres que celles contenant des radicaux ester sulfonique ou ester sulfurique ou ayant la structure des unités récurrentes C ou D.



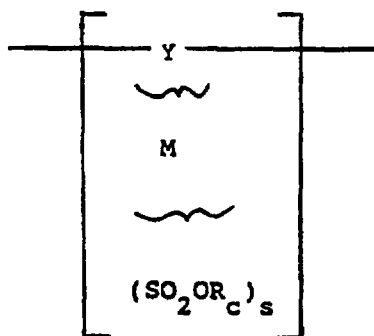
36. Polymère suivant la revendication 35, dans lequel le polymère comprend 5 à 97 moles % d'unités récurrentes E.
37. Polymère suivant la revendication 35 ou 36, dans lequel les unités récurrentes E dérivent d'un ou plusieurs monomères choisis parmi les esters et amides d'acides carboxyliques oléfiniquement insaturés, les monooléfines alpha-aryl-substituées, les esters vinyliques, les halogénures de vinyle, les halogénures de vinylidène et les nitriles oléfiniquement insaturés.
38. Polymère suivant la revendication 37, dans lequel les unités récurrentes E dérivent d'un ou plusieurs monomères choisis parmi l'acrylate de méthyle, le méthacrylate de méthyle, l'acrylate d'éthyle, le méthacrylate d'éthyle, l'acrylate de n-butyle, l'acrylamide, le méthacrylamide, le styrène, l'alpha-méthylstyrène, le chlorure de vinyle, le chlorure de vinylidène, l'acrylonitrile et le méthacrylonitrile.
39. Polymère suivant l'une quelconque des revendications 22 à 38, dans lequel le polymère comprend 3 à 40 moles % d'une ou plusieurs unités récurrentes A, 0 à 40 moles % d'une ou plusieurs unités récurrentes C, 0 à 20 moles % d'une ou plusieurs unités récurrentes D et 5 à 97 moles % d'une ou plusieurs unités récurrentes E.
40. Polymère suivant l'une quelconque des revendications 22 à 39, dans lequel le polymère a un poids moléculaire moyen en masse (M_m) de l'intervalle de 50.000 à 300.000.
41. Procédé de traitement d'une surface, lequel procédé comprend l'application, sur la surface, d'une composition de revêtement érodable par l'eau suivant l'une quelconque des revendications 1 à 21 de manière à former sur la surface un revêtement érodable par l'eau.
42. Procédé de production d'un polymère érodable par l'eau, lequel procédé comprend la polymérisation de monomères comprenant au moins un monomère de formule $\text{CH}_2=\text{CHMSO}_2\text{G}$, l'au moins un monomère étant utilisé en une quantité apportant 3 à 40 moles % d'unités récurrentes qui en dérivent dans le polymère final, où :
- G est un radical aisé à convertir par une réaction d'estérification en un radical $-\text{OR}_c$ après polymérisation;
- R_c est un radical choisi parmi les radicaux alcoyle (notamment alcoyle primaire, secondaire et tertiaire et cycloalcoyle), aryle, alcaryle, aralcoyle, alcénoxyalcoyle et poly(alcénoxy)alcoyle;
- M est un lien direct ou un radical choisi parmi les radicaux $-(\text{alcoylène})-$, $-\text{CO}-\text{O}-(\text{alcoylène})-$, $-\text{CO}-\text{NH}-(\text{alcoylène})-$, $-\text{NH}-\text{CO}-(\text{alcoylène})-$, $-(\text{arylène})-$, $-(\text{alcoylène})-(\text{arylène})-$, $-(\text{alcoylène})-\text{O}-(\text{alcoylène})-$, $-(\text{alcoylène})-\text{O}-(\text{arylène})-$, $-(\text{arylène})-\text{O}-(\text{arylène})-$, $-(\text{arylène})-\text{O}-(\text{alcoylène})-$, $-\text{alcoylénoxy}-$ et $-\text{polyalcoylénoxy}-$;
- et ensuite l'exécution d'une réaction d'estérification à l'aide d'un composé de formule R_cOH .
43. Procédé suivant la revendication 42, dans lequel G est Cl.
44. Procédé suivant la revendication 42 ou 43, dans lequel M est p-phénylène.
45. Procédé suivant l'une quelconque des revendications 42 à 44, dans lequel R_c est alcoyle de 1 à 20 atomes de carbone.
46. Procédé suivant la revendication 45, dans lequel R_c est méthyle.
47. Procédé suivant l'une quelconque des revendications 42 à 46, dans lequel l'estérification est exécutée en présence de triéthylamine.
48. Polymère érodable par l'eau formé par un procédé suivant l'une quelconque des revendications 42 à 47.

55 Patentansprüche

1. Beschichtungszusammensetzung zur Behandlung einer Oberfläche, um darauf eine durch Wasser erodierbare Beschichtung zu erzeugen, welche Zusammensetzung mindestens ein erodierbares Poly-

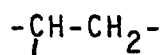


mer enthält, das 3 bis 40 Mol % einer oder mehrerer Wiederholungseinheiten A enthält, von denen jede mindestens eine hydrolysierbare Sulfonatester-Gruppe aufweist, die vom Hauptgerüst des Polymers abstammt, wobei die Wiederholungseinheit A die Formel

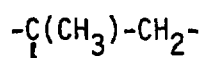


aufweist, worin

Y, welches in den Wiederholungseinheiten A der Formel I gleich oder unterschiedlich sein kann, für eine Gruppe im Hauptgerüst steht, die aus



und



ausgewählt ist;

s für eine Ganzzahl von 1 oder mehr steht, und zwar entsprechend der Anzahl der SO_2OR_c -Gruppen in der Wiederholungseinheit A der Formel I;

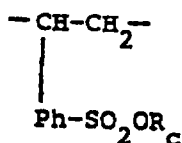
R_c , welches in der gleichen Wiederholungseinheit A der Formel I (wenn s für 2 oder mehr steht) oder in unterschiedlichen Wiederholungseinheiten A der Formel I gleich oder verschieden sein kann, für eine Gruppe steht, die ausgewählt ist aus einer oder mehreren Alkyl- (einschließlich primären, sekundären und tertiären Alkyl- und Cycloalkyl-), Aryl-, Alkaryl-, Aralkyl-, Alkenoxyalkyl- und Poly(alkenoxo)alkyl-Gruppen;

wobei jede SO_2OR_c -Gruppe über ein Zwischenglied M an die Gruppe Y gebunden ist, und wobei M für eine direkte Bindung oder eine Gruppe steht, die ausgewählt ist aus -(Alkylen)-, -CO-O-(Alkylen)-, -CO-NH-(Alkylen)-, -NH-CO-(Alkylen)-, -(Arylen)-, -(Alkylen)-(arylen)-, -(Alkylen)-O-(alkylen), -(Alkylen)-O-(arylen)-, -(Arylen)-O-(arylen), -(Arylen)-O-(alkylen)-, Alkylenoxy- und Polyalkylenoxy-Gruppen.

2. Beschichtungszusammensetzung nach Anspruch 1, bei welcher M ausgewählt ist aus einer oder mehreren o-, m- oder p-Phenyl-Gruppen.
3. Beschichtungszusammensetzung nach Anspruch 1 oder 2, bei welcher s für 1 steht.
4. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, bei welcher R_c ausgewählt ist aus einer oder mehreren Alkyl- (mit 1 bis 20 Kohlenstoffatomen), Phenyl- und Benzyl-Gruppen.
5. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, bei welcher die Wiederholungseinheit A die Formel



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aufweist, worin -PH- für p-Phenylen steht.

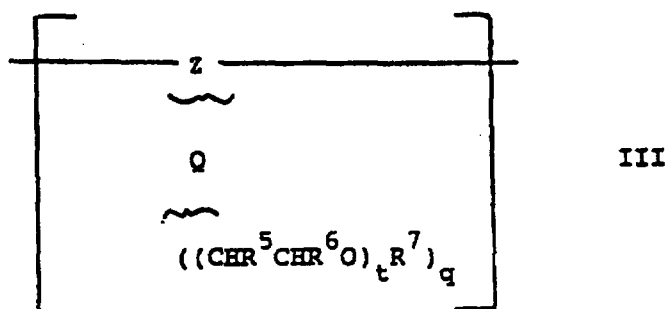
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6. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, bei welcher das durch Wasser erodierbare Polymer zusätzlich ein oder mehrere Wiederholungseinheiten C enthält, die mindestens eine Alkylenoxid- oder Poly(alkylenoxid)-Gruppe und keine Sulfonatester- oder Sulfatester-Gruppe enthalten, wobei die Wiederholungseinheit C die Formel

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aufweist, worin

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t für eine Ganzzahl von 1 bis 200 steht;

q für eine Ganzzahl von 1 bis 4 steht;

Z, welches in den Wiederholungseinheiten C der Formel III gleich oder unterschiedlich sein kann, für einen Kohlenwasserstoff-Rest oder ein substituiertes Derivat davon steht;

35

R⁵, welches in der gleichen Wiederholungseinheit C der Formel III (wenn t oder q für 2 oder mehr steht) oder in unterschiedlichen Wiederholungseinheiten C der Formel III gleich oder verschieden sein kann, für Wasserstoff oder Methyl steht;

R⁶, welches in der gleichen Wiederholungseinheit C der Formel III (wenn t oder q für 2 oder mehr steht) oder in unterschiedlichen Wiederholungseinheiten C der Formel III gleich oder verschieden sein kann, für Wasserstoff oder Methyl steht;

40

mit der Maßgabe, daß R⁵ und R⁶ in einer einzelnen Einheit (CHR⁵CHR⁶O) nicht beide Methyl sein können;

R⁷, welches in der gleichen Wiederholungseinheit C der Formel III (wenn q für 2 oder mehr steht) oder in unterschiedlichen Wiederholungseinheiten C der Formel III gleich oder verschieden sein kann, für Wasserstoff, eine Alkyl-Gruppe oder eine Acyl-Gruppe steht;

45

wobei jede (CHR⁵CHR⁶O)_t-Gruppe über ein oder mehrere Zwischenglieder Q an den Kohlenwasserstoff-Rest Z gebunden ist und in solchen Fällen, in denen q für 2 bis 4 steht, durch Q an das gleiche oder an unterschiedliche Kohlenstoffatome von Z gebunden sein kann; und wobei Q für ein oder mehrere Zwischenglieder steht und Q in den Wiederholungseinheiten C der Formel III gleich oder unterschiedlich sein kann und ausgewählt ist aus ein oder mehreren direkten Bindungen und ein oder mehreren Atomen oder Atomgruppen, die eine Kette von einem oder mehreren Atomen zur Verbindung einer (CHR⁵CHR⁶O)_t-Gruppe mit Z ergeben, mit der Maßgabe, daß mehr als zwei (CHR⁵CHR⁶O)_t-Gruppen nicht direkt an das gleiche Kohlenstoffatomen in Z gebunden sein können, sofern dieses Kohlenstoffatom einen Teil des Hauptkettenpolymergerüsts bildet.

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7. Beschichtungszusammensetzung nach Anspruch 6, bei welcher q für 1 oder 2 steht.

8. Beschichtungszusammensetzung nach Anspruch 6 oder 7, bei welcher t für 1 bis 60 steht.



9. Beschichtungszusammensetzung nach einem der Ansprüche 6 bis 8, bei welcher die Wiederholungseinheit C die Formel

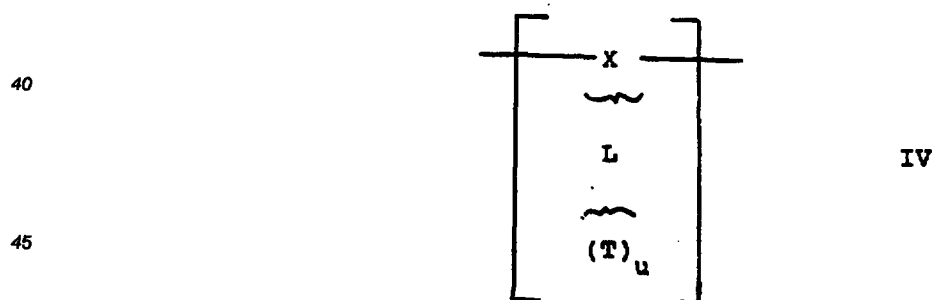


oder



aufweist.

10. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, bei welcher das erodierbare Polymer 0 bis 50 Mol-% Wiederholungseinheiten C enthält.
11. Beschichtungszusammensetzung nach Anspruch 10, bei welcher das erodierbare Polymer 0 bis 40 Mol-% Wiederholungseinheiten C enthält.
12. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, bei welcher das erodierbare Polymer zusätzlich ein oder mehrere Wiederholungseinheiten D enthält, die mindestens eine saure und/oder basische Gruppe enthalten, wobei die Wiederholungseinheit D die Formel



aufweist, worin

X, welches in der Wiederholungseinheit D der Formel IV gleich oder unterschiedlich sein kann, für einen Kohlenwasserstoff-Rest oder ein substituiertes Derivat davon steht;
u für eine Ganzzahl von 1 bis 4 steht;

T, welches in den Wiederholungseinheiten D der Formel IV gleich oder unterschiedlich sein kann, für eine Gruppe steht, die einen sauren oder basischen Substituenten (mit Ausnahme eines Substituenten, der durch Sulfonat- oder Sulfatesterhydrolyse erhältlich ist) trägt;

wobei jede Gruppe T über ein oder mehrere Zwischenglieder L an den Kohlenwasserstoff-Rest X gebunden ist und in Fällen, bei denen u für 2 bis 4 steht, durch L an das gleiche oder an

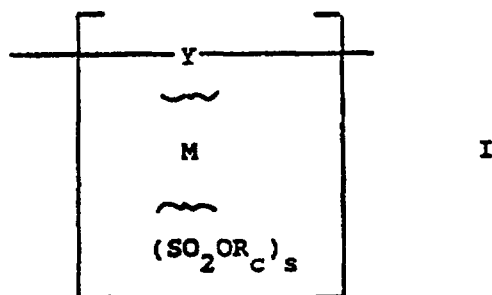


unterschiedliche Kohlenstoffatome von X gebunden sein kann; und

wobei L für ein oder mehrere Zwischenglieder steht und L in den Wiederholungseinheiten D der Formel IV gleich oder unterschiedlich sein kann und ausgewählt ist aus ein oder mehreren direkten Bindungen und ein oder mehreren Atomen oder Atomgruppen, die eine Kette von ein oder mehreren Atomen für die Verbindung einer Gruppe T mit X bilden, mit der Maßgabe, daß mehr als zwei Gruppen T nicht direkt an das gleiche Kohlenstoffatom in X gebunden sein können, wenn dieses Kohlenstoffatom einen Teil des Hauptkettenpolymergerüsts bildet.

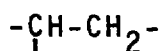
13. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, bei welcher das erodierbare Polymer 0 bis 30 % Wiederholungseinheiten D enthält.
14. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, bei welcher das erodierbare Polymer zusätzlich ein oder mehrere Wiederholungseinheiten E enthält, wobei die Wiederholungseinheiten andere als solche sind, die Sulfonatester- oder Sulfatester-Gruppen enthalten oder die Struktur der Wiederholungseinheiten C oder D besitzen.
15. Beschichtungszusammensetzung nach Anspruch 14, bei welcher das erodierbare Polymer 5 bis 97 Mol-% Wiederholungseinheiten E enthält.
16. Beschichtungszusammensetzung nach Anspruch 14 oder 15, bei welcher die Wiederholungseinheiten E sich von ein oder mehreren Monomeren ableiten, die ausgewählt sind aus Estern und Amiden von olefinisch ungesättigten Carbonsäuren, α -aryl-substituierten Monoolefinen, Vinylestern, Vinylhalogeniden, Vinylidenhalogeniden und olefinisch ungesättigten Nitrilen.
17. Beschichtungszusammensetzung nach Anspruch 16, bei welcher die Wiederholungseinheiten E sich von ein oder mehreren Monomeren ableiten, die ausgewählt sind aus Methylacrylat, Methylmethacrylat, Ethylacrylat, Ethylmethacrylat, n-Butylacrylat, Acrylamid, Methacrylamid, Styrol, α -Methylstyrol, Vinylchlorid, Vinylidenchlorid, Acrylonitril und Methacrylonitril.
18. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, bei welcher das erodierbare Polymer 3 bis 40 Mol-% ein oder mehrerer Wiederholungseinheiten A, 0 bis 40 Mol-% ein oder mehrerer Wiederholungseinheiten C, 0 bis 20 Mol-% ein oder mehrerer Wiederholungseinheiten D und 5 bis 97 Mol-% ein oder mehrerer Wiederholungseinheiten E enthält.
19. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, bei welcher das erodierbare Polymer ein gewichtsmäßiges Durchschnittsmolekulargewicht (M_w) im Bereich von 50 000 bis 300 000 aufweist.
20. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche in Form einer Anstrichzusammensetzung auf der Basis von Wasser oder einer organischen Flüssigkeit, welche mindestens ein Pigment enthält.
21. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, welche mindestens ein Biocid enthält.
22. Durch Wasser erodierbares Polymer, welches 3 bis 40 Mol-% einer oder mehrerer Wiederholungseinheiten A enthält, von denen jede mindestens eine hydrolysierbare Sulfonatester-Gruppe aufweist, die vom Hauptgerüst des Polymers absteht, wobei die Wiederholungseinheit A



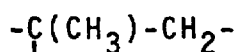


aufweist, worin

Y, welches in den Wiederholungseinheiten A der Formel I gleich oder unterschiedlich sein kann, für eine Gruppe im Hauptgerüst steht, die aus



und



ausgewählt ist:

s für eine Ganzzahl von 1 oder mehr steht, und zwar entsprechend der Anzahl der SO_2OR_6 -Gruppen in der Wiederholungseinheit A der Formel I;

R₆, welches in der gleichen Wiederholungseinheit A der Formel I (wenn s für 2 oder mehr steht) oder in unterschiedlichen Wiederholungseinheiten A der Formel I gleich oder verschieden sein kann, für eine Gruppe steht, die ausgewählt ist aus einer oder mehreren Alkyl- (einschließlich primären, sekundären und tertiären Alkyl- und Cycloalkyl-), Aryl-, Alkaryl-, Araalkyl-, Alkenoxyalkyl- und Poly(alkenoxy)alkyl-Gruppen;

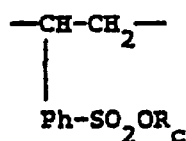
wobei jede SO_2OR_c -Gruppe über ein Zwischenglied M an die Gruppe Y gebunden ist, und wobei M für eine direkte Bindung oder eine Gruppe steht, die ausgewählt ist aus $-(\text{Alkyl})-$, $-\text{CO}-\text{O}-(\text{Alkyl})-$, $-\text{CO}-\text{NH}-(\text{Alkyl})-$, $-\text{NH}-\text{CO}-(\text{Alkyl})-$, $-(\text{Aryl})-$, $-(\text{Alkyl})-(\text{aryl})-$, $-(\text{Alkyl})-\text{O}-(\text{alkyl})-$, $-(\text{Alkyl})-\text{O}-(\text{aryl})-$, $-(\text{Aryl})-\text{O}-(\text{aryl})-$, $-(\text{Aryl})-\text{O}-(\text{alkyl})-$, $-\text{Alkylenoxy}-$ und $\text{Polyalkylenoxy}-$ Gruppen.

23. Polymer nach Anspruch 22, bei welchem M ausgewählt ist aus einer oder mehreren o-, m- oder p-Phenylen-Gruppen.

24. Polymer nach Anspruch 22 oder 23, bei welchem s für 1 steht.

25. Polymer nach einem der Ansprüche 22 bis 24, bei welchem R_c ausgewählt ist aus einer oder mehreren Alkyl- (mit 1 bis 20 Kohlenstoffatomen), Phenyl- und Benzyl-Gruppen.

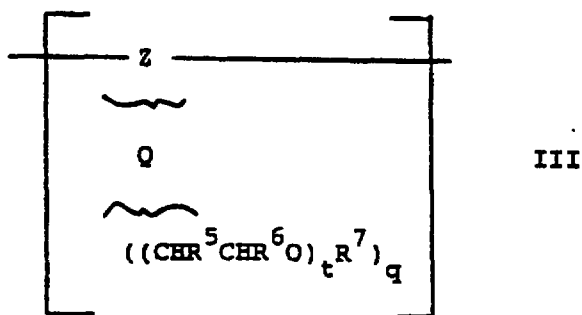
26. Polymer nach einem der Ansprüche 22 bis 25, bei welchem die Wiederholungseinheit A die Formel



aufweist, worin -PH- für p-Phenylen steht.



27. Polymer nach einem der Ansprüche 22 bis 26, bei welchem das Polymer zusätzlich ein oder mehrere Wiederholungseinheiten C enthält, die mindestens eine Alkylendio- oder Poly(alkylendio)-Gruppe und keine Sulfonatester- oder Sulfatester-Gruppe enthalten, wobei die Wiederholungseinheit C die Formel



aufweist, worin

t für eine Ganzzahl von 1 bis 200 steht;

q für eine Ganzzahl von 1 bis 4 steht;

Z, welches in den Wiederholungseinheiten C der Formel III gleich oder unterschiedlich sein kann, für einen Kohlenwasserstoff-Rest oder ein substituiertes Derivat davon steht;

R⁵, welches in der gleichen Wiederholungseinheit C der Formel III (wenn t oder q für 2 oder mehr steht) oder in unterschiedlichen Wiederholungseinheiten C der Formel III gleich oder verschieden sein kann, für Wasserstoff oder Methyl steht;

R⁶, welches in der gleichen Wiederholungseinheit C der Formel III (wenn t oder q für 2 oder mehr steht) oder in unterschiedlichen Wiederholungseinheiten C der Formel III gleich oder verschieden sein kann, für Wasserstoff oder Methyl steht;

mit der Maßgabe, daß R⁵ und R⁶ in einer einzelnen Einheit (CHR⁵CHR⁶O) nicht beide Methyl sein können;

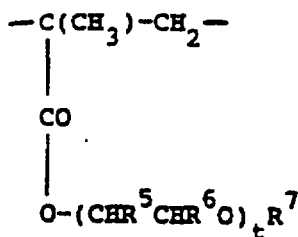
R⁷, welches in der gleichen Wiederholungseinheit C der Formel III (wenn q für 2 oder mehr steht) oder in unterschiedlichen Wiederholungseinheiten C der Formel III gleich oder verschieden sein kann, für Wasserstoff, eine Alkyl-Gruppe oder eine Acyl-Gruppe steht;

wobei jede (CHR⁵CHR⁶O)_t-Gruppe über ein oder mehrere Zwischenglieder Q an den Kohlenwasserstoff-Rest Z gebunden ist und in solchen Fällen, in denen q für 2 bis 4 steht, durch Q an das gleiche oder an unterschiedliche Kohlenstoffatome von Z gebunden sein kann; und wobei Q für ein oder mehrere Zwischenglieder steht und Q in den Wiederholungseinheiten C der Formel III gleich oder unterschiedlich sein kann und ausgewählt ist aus ein oder mehreren direkten Bindungen und ein oder mehreren Atomen oder Atomgruppen, die eine Kette von einem oder mehreren Atomen zur Verbindung einer (CHR⁵CHR⁶O)_t-Gruppe mit Z ergeben, mit der Maßgabe, daß mehr als zwei (CHR⁵CHR⁶O)_t-Gruppen nicht direkt an das gleiche Kohlenstoffatom in Z gebunden sein können, sofern dieses Kohlenstoffatom einen Teil des Hauptkettenpolymergerüsts bildet.

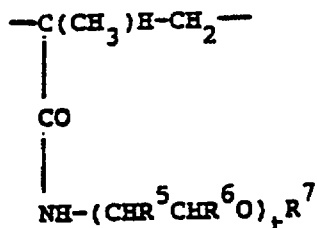
28. Polymer nach Anspruch 27, bei welchem q für 1 oder 2 steht.

29. Polymer nach einem der Ansprüche 27 oder 28, bei welchem t für 1 bis 60 steht.

30. Polymer nach einem der Ansprüche 27 bis 29, bei welchem die Wiederholungseinheit C die Formel

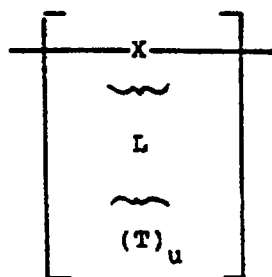


oder



aufweist.

31. Polymer nach einem der Ansprüche 22 bis 30, bei welchem das erodierbare Polymer 0 bis 50 Mol-% Wiederholungseinheiten C enthält.
32. Polymer nach Anspruch 31, bei welchem das Polymer 0 bis 40 Mol-% Wiederholungseinheiten C enthält.
33. Polymer nach einem der Ansprüche 22 bis 32, bei welchem das Polymer zusätzlich einen oder mehrere Wiederholungseinheiten D enthält, die mindestens eine saure und/oder basische Gruppe enthalten, wobei die Wiederholungseinheit D die Formel



IV

aufweist, worin

X, welches in der Wiederholungseinheit D der Formel IV gleich oder unterschiedlich sein kann, für einen Kohlenwasserstoff-Rest oder ein substituiertes Derivat davon steht;

u für eine Ganzzahl von 1 bis 4 steht;

T, welches in den Wiederholungseinheiten D der Formel IV gleich oder unterschiedlich sein kann, für eine Gruppe steht, die einen sauren oder basischen Substituenten (mit Ausnahme eines Substituenten, der durch Sulfonat- oder Sulfatesterhydrolyse erhältlich ist) trägt;

wobei jede Gruppe T über ein oder mehrere Zwischenglieder L an den Kohlenwasserstoff-Rest X gebunden ist und in Fällen, bei denen u für 2 bis 4 steht, durch L an das gleiche oder an unterschiedliche Kohlenstoffatome von X gebunden sein kann; und

wobei L für ein oder mehrere Zwischenglieder steht und L in den Wiederholungseinheiten D der Formel IV gleich oder unterschiedlich sein kann und ausgewählt ist aus ein oder mehreren direkten Bindungen und ein oder mehreren Atomen oder Atomgruppen, die eine Kette von ein oder mehreren Atomen für die Verbindung einer Gruppe T mit X bilden, mit der Maßgabe, daß mehr als zwei Gruppen T nicht direkt an das gleiche Kohlenstoffatom in X gebunden sein können, wenn dieses Kohlenstoffatom einen Teil des Hauptkettenpolymergerüsts bildet.

34. Polymer nach einem der Ansprüche 22 bis 33, bei welchem das Polymer 0 bis 30 Mol-% Wiederholungseinheiten D enthält.

35. Polymer nach einem der Ansprüche 22 bis 34, bei welchem das Polymer zusätzlich ein oder mehrere Wiederholungseinheiten E enthält, wobei die Wiederholungseinheiten andere als solche sind, die



Sulfonatester- oder Sulfatester-Gruppen enthalten oder die Struktur der Wiederholungseinheiten C oder D besitzen.

36. Polymer nach Anspruch 35, bei welchem das Polymer 5 bis 97 Mol % Wiederholungseinheiten E enthält.
37. Polymer nach Anspruch 35 oder 36, bei welchem die Wiederholungseinheiten E sich von ein oder mehreren Monomeren ableiten, die ausgewählt sind aus Estern und Amiden von olefinisch ungesättigten Carbonsäuren, α -aryl-substituierten Monoolefinen, Vinylestern, Vinylhalogeniden, Vinylidenhalogeniden und olefinisch ungesättigten Nitrilen.
38. Polymer nach Anspruch 37, bei welchem die Wiederholungseinheiten E sich von ein oder mehreren Monomeren ableiten, die ausgewählt sind aus Methylacrylat, Methylmethacrylat, Ethylacrylat, Ethylmethacrylat, n-Butylacrylat, Acrylamid, Methacrylamid, Styrol, α -Methylstyrol, Vinylchlorid, Vinylidenchlorid, Acrylonitril und Methacrylonitril.
39. Polymer nach einem der Ansprüche 22 bis 38, bei welchem das Polymer 3 bis 40 Mol-% ein oder mehrerer Wiederholungseinheiten A, 0 bis 40 Mol-% ein oder mehrerer Wiederholungseinheiten C, 0 bis 20 Mol-% ein oder mehrerer Wiederholungseinheiten D und 5 bis 97 Mol-% ein oder mehrerer Wiederholungseinheiten E enthält.
40. Polymer nach einem der Ansprüche 22 bis 39, bei welchem das Polymer ein gewichtsmäßiges Durchschnittsmolekulargewicht (M_w) im Bereich von 50 000 bis 300 000 aufweist.
41. Verfahren zur Behandlung einer Oberfläche, bei welchem auf die Oberfläche eine durch Wasser erodierbare Beschichtungszusammensetzung nach einem der Ansprüche 1 bis 21 aufgebracht wird, um auf der Oberfläche eine durch Wasser erodierbare Beschichtung zu bilden.
42. Verfahren zur Herstellung eines durch Wasser erodierbaren Polymers, bei welchem Monomere polymerisiert werden, die mindestens ein Monomer der Formel $\text{CH}_2 = \text{CHMSO}_2\text{G}$ umfassen, wobei dieses mindestens ein Monomer in einer Menge verwendet wird, um 3 bis 40 Mol % davon abgeleitete Wiederholungseinheiten im endgültigen Monomer zu bilden, worin:
- G für eine Gruppe steht, die nach der Polymerisation leicht durch eine Veresterungsreaktion in eine $-\text{OR}_c$ -Gruppe umwandelbar ist;
 - R_c für eine Gruppe steht, die ausgewählt ist aus Alkyl-(einschließlich primären, sekundären und tertiären Alkyl- und Cycloalkyl-), Aryl-, Alkaryl-, Aralkyl-, Alkenoxyalkyl- und Poly(alkenoxy)-alkyl-Gruppen; und
 - M für eine direkte Bindung oder eine Gruppe steht, die ausgewählt ist aus $-(\text{Alkyl})-$, $-\text{CO}-\text{O}-(\text{Alkyl})-$, $-\text{CO}-\text{NH}-(\text{Alkyl})-$, $-\text{NH}-\text{CO}-(\text{Alkyl})-$, $-(\text{Aryl})-$, $-(\text{Alkyl})-(\text{aryl})-$, $-(\text{Alkyl})-\text{O}-(\text{alkyl})-$, $-(\text{Alkyl})-\text{O}-(\text{aryl})-$, $-(\text{Aryl})-\text{O}-(\text{aryl})-$, $-(\text{Aryl})-\text{O}-(\text{alkyl})-$, Alkylendioxy- und -Polyalkylendioxy-Gruppen;
- worauf dann unter Verwendung einer Verbindung der Formel $R_c\text{OH}$ eine Veresterungsreaktion ausgeführt wird.
43. Verfahren nach Anspruch 42, bei welchem G für Cl steht.
44. Verfahren nach Anspruch 42 oder 43, bei welchem M für p-Phenyl steht.
45. Verfahren nach einem der Ansprüche 42 bis 44, bei welchem R_c für Alkyl mit 1 bis 20 Kohlenstoffatomen steht.
46. Verfahren nach Anspruch 45, bei welchem R_c für Methyl steht.
47. Verfahren nach einem der Ansprüche 42 bis 46, bei welchem die Veresterung in Gegenwart von Triethylamin ausgeführt wird.
48. Durch Wasser erodierbares Polymer, welches durch ein Verfahren nach einem der Ansprüche 42 bis 47 hergestellt worden ist.

