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PROCESS FOR ELECTROLYTICALLY APPLYING POLYMER COATINGS ON ELECTROCONDUCTIVE ARTICLES

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No Drawing. Continuation of abandoned application Ser. No. 879,510, Nov. 24, 1969. This application July 6, 1971, Ser. No. 160,222

Int. Cl. C23b 5/00; B01k 5/00, 1/00

U.S. Cl. 204—14 N 9 Claims

ABSTRACT OF THE DISCLOSURE

Hydrophobic polymer coatings are applied to solid electroconductive articles by subjecting a polysulfonium salt in solution in an electrolysis solvent to an electrical potential sufficient to reduce the sulfonium salt. The solid electroconductive articles are used as the cathode in the electrolysis process. In example, a lead electrode is coated with poly(p-xylylene) by electrolyzing an aqueous solution of (p-phenylenedimethylene)bis(dimethylsulfonium chloride).

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of our U.S. patent application S.N. 879,510, filed Nov. 24, 1969 (now abandoned), which in turn is a continuation-in-part of our U.S. patent applications S.N. 647,895 and 647,896, both filed June 22, 1967. The latter applications are now U.S. Pat. 3,480,525 and U.S. Pat. 3,480,527.

BACKGROUND OF THE INVENTION

A process for preparing poly(p-xylylene) by electrochemical reduction of sulfonium salts, such as α,α-bis(dimethyl sulfonium chloride)-p-xylene, in various electrolysis solvents, such as water, was described in our copending U.S. patent application, Ser. No. 647,895. The process comprised subjecting a solution of said sulfonium salts to an electrical potential sufficient to reduce the sulfonium salt. The poly(p-xylylene) thus prepared coated various metallic cathodes in the electrolysis process, namely aluminum, tin and lead. The process was operable at both controlled and uncontrolled electrical potentials, i.e., the cathode potential is, respectively, maintained at a constant value (volts), or allowed to vary from the initial cathode potential towards a more negative voltage as the cathode is coated and the current ceases to flow in the electrolysis cell.

The polarography of sulfonium salts is known, as described by Colichman and Love, J. Org. Chem., 18, 40 (1953). They used a stirred mercury cathode and a very carefully monitored cathode potential. However, the coating phenomena on solid electroconductive materials was unknown until our discovery thereof.

The subject invention pertains to an electrochemical reduction of organic polysulfonium salts to form protective, decorative and otherwise useful coatings on solid electroconductive articles. Said reduction requires an electrolysis system comprising an anode, a cathode, an electrolysis solvent and a means for establishing and maintaining an electrical potential between said anode and cathode.

SUMMARY OF THE INVENTION

It has now been discovered that solid electroconductive articles can be easily coated with a polymeric material by using such electroconductive articles as the cathode in the above described electrolysis system and subjecting a polysulfonium salt in solution in the electrolysis solvent to an electrical potential sufficient to reduce the polysulfonium salt.

The importance of this invention resides in the fact that the soluble polysulfonium salts can be electrolytically converted to insoluble polymers on the surface of many articles regardless of their size or shape. The subject coatings are generally obtained as a thin film which adheres to the cathode surface. These coatings can and do impart desirable properties to the coated substrate, such as electrical insulation for wiring, corrosion, and oxidation protection for metal parts, abrasion-resistant surfaces for working parts subject to wear, and so on. Decorative or colored coatings can also be applied in accordance with this invention, e.g., an article may be obtained having an orange-peel effect on the surface, or a high gloss or color may be obtained (the color resulting from a chromophore(s) in the polymer structure). The physical properties of the coating will vary depending upon the particular polysulfonium salt(s) chosen, but, the coatings are generally infusible and hydrophobic, particularly when the coated cathode is subsequently heated to a temperature which thermally decomposes any residual sulfonium groups and evaporates any entrained solvent.

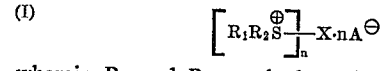
Suitable polysulfonium salts in this reaction may range in molecular weight from monomers to high polymers.

The lower molecular weight salts can be electroreductively coupled during the deposition process to give higher molecular weight products. These products can then be converted to even higher molecular weight or crosslinked products by subsequent curing.

The higher molecular weight salts on the other hand need only to be insolubilized at the cathode surface by electrolytically destroying some or all of the sulfonium moieties responsible for its solubility. The properties of such a coating may be further enhanced by an increase in molecular weight pursuant to chain-extending or crosslinking arising as a consequence of a reductive coupling reaction.

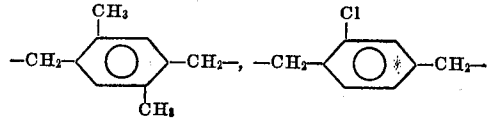
The polysulfonium salts suitable in the subject invention are substantially soluble in the electrolysis solvent and have the general structural formula

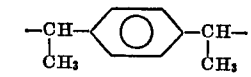
(I)

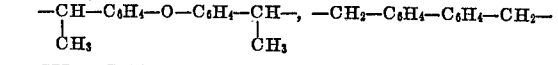


wherein R_1 and R_2 are hydrocarbon or hydroxy-substituted hydrocarbon groups of 1 to about 30 carbon atoms; n is an integer and is at least 2; X is an n-valent hydrocarbon radical and is preferably an activating hydrocarbon radical (i.e., a radical which causes preferential cleavage of the +S—X bond) whose chain length may be interrupted by oxygen, sulfur or nitrogen, or by a keto, ester or amide linkage; and $A^{\ominus}$ is an electrolytically acceptable anion, and is typically the anion of an acid, such as hydroxide, chloride, bromide, nitrate, sulfate, bicarbonate, phosphate, acetate, maleate, benzoate and the like.

X in (I) above includes: polymethylene (aryl) radicals, such as $C_6H_4(CH_2)_2$, $C_6H_3(CH_2)_3$,

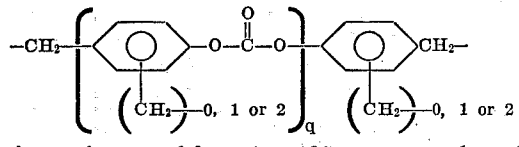




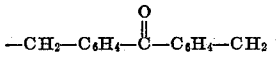


$-CH_2-C_6H_4-CH_2CH_2-C_6H_4CH_2-$, polysulfoniums prepared from halomethylated polystyrene or α-methyl-

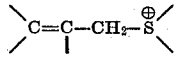
styrene and the like; polymethylene (polyarylene oxides and sulfides), such as the polysulfoniums prepared by reacting a dialkyl sulfide, e.g., dimethyl sulfide, with di-, tri- and/or tetra-chloromethylated diphenyl oxide or sulfide polysulfoniums from halomethylated polyphenylene oxide, and the like; polymethylene (polyarylene carbonates), such as



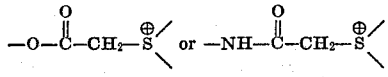
q being an integer of from 1 to 100 or more; polymethylene (aromatic polyesters and polyamides), such as the polysulfoniums prepared by reacting a dialkyl sulfide with the chloromethylated polyester or polyamide of terephthalic acid and ethylene glycol or hexamethylenediamine, and the like; aromatic ketone radicals, such as



and the like; and other activating radicals, such as: polyallylic and substituted allylic radicals, i.e., polymers having pendant and/or terminal



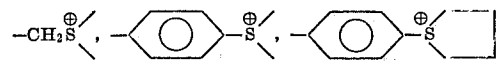
wherein the vinyl group may be included in the polymer backbone or may be a side chain; polyradicals derived from polyols and polyamines by reacting α-haloacetic acid with such polyols and polyamines to give the corresponding α-haloacetates and α-haloacetamides and thereafter preparing the polysulfonium salts having terminal and/or pendant



groups; polyradicals derived by removal of chlorine atoms from polymers and copolymers of vinylbenzyl chloride;

polyradicals derived from polymers and copolymers of 2-chloromethyl-1,3-butadiene; and other like groups having 2 or more activated ⊕S—X bonds. An activated radical therefore includes those groups having an aromatic, olefinic or acyl radical attached to a methylene carbon which is in turn attached to the sulfonium sulfur atom.

X in (I) above also includes non-activated hydro carbon radicals, such as alkylene or arylene disulfoniums, and hydrocarbons having terminal and/or pendant polysulfonium groups, such as polyalkylenepolysulfoniums; e.g., polyethylene, polyvinyl chloride, polystyrene, and the like, having pendant



and other like groups. Other non-activated radicals include the polysulfoniums made from polyalkylene sulfides and polyarylene sulfides by reacting them with methyl iodide, benzyl chloride, etc. Preferred polysulfonium salts are water-soluble salts including those of Formula I wherein: R_1 and R_2 are hydrocarbon or hydroxy-substituted hydrocarbon groups of 1 to about 10 carbon atoms, and most preferably 1 to about 4 carbon atoms; X is polymethylene(aryl) or substituted polymethylene(aryl), polymethylene(polyarylene oxide or sulfide), particularly those of the formula —CH_2—CH_6H_4—CH_2—,

—CH_2—C_6H_4—C_6H_4—CH_2

—$CH_2C_6H_4$—Y—C_6H_4—CH_2— wherein Y is oxygen or sulfur or alkylene, arylene or alkenylene of 1 to about 10 carbon atoms, and polysulfonium salts obtained by the reaction of chloromethylated polystyrene with sulfides and polysulfonium salts obtained by the reaction of copolymers of vinylbenzyl chloride and other vinyls or vinylidene, acrylic, methacrylate, maleate monomers with sulfides. Further representative examples of suitable such polysulfonium salts include those of Formula I wherein:

TABLE I

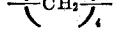
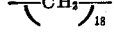
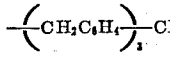
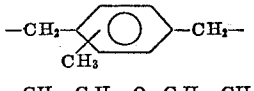
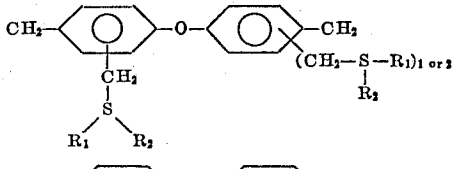
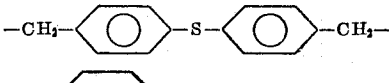
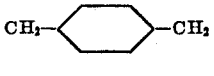
R_1	R_2	X	n	A^-
CH_3	CH_3	—CH_2CH_2—	2	Cl.
C_2H_5	C_2H_5		2	Br.
C_2H_4OH	C_2H_4OH		2	F.
CH_3	CH_3	—CH_2—C_6H_4—CH_2—	2	NO_3.
n-C_4H_9	n-C_4H_9	—CH_2—C_6H_4—C_6H_4—CH_2	2	Tosylate.
CH_3	C_2H_5		3	Cl.
n-$(CH_2)_5CH_2OH$	n-$(CH_2)_5CH_2OH$		2	Br.
n-$C_{10}H_{21}$	n-$C_{10}H_{21}$	—CH_2—C_6H_4—O—C_6H_4—CH_2—	2	F.
C_2H_4OH	C_2H_4OH	—CH_2—C_6H_3Cl—O—C_6H_3Cl—CH_2—	2	OH.
CH_3	CH_3	—CH_2—$C_6H_4(CH_2)_2C_6H_4$—CH_2—	2	Tosylate.
C_2H_4OH	C_2H_4OH		3 or 4	Cl.
n-$C_{18}H_{37}$	n-$C_{18}H_{37}$		2	Tosylate.
n-C_6H_{13}	n-C_6H_{13}		2	Do.

TABLE I—Continued

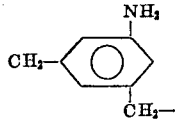
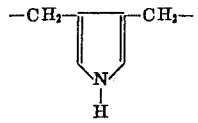
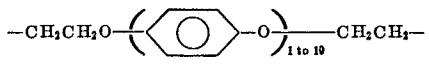
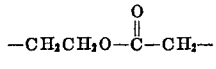
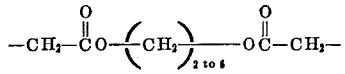
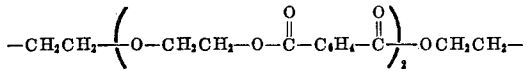
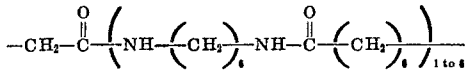
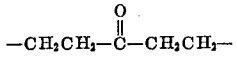
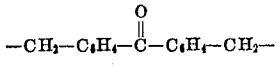
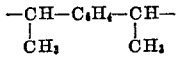
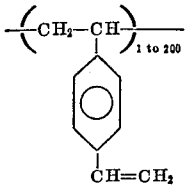
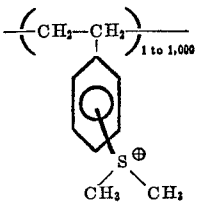
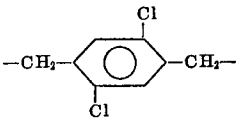
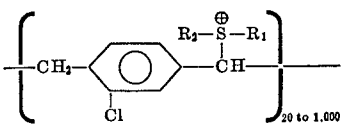
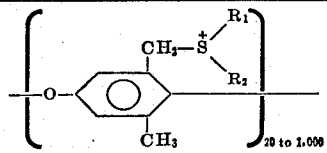
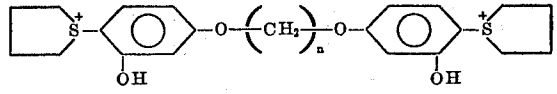
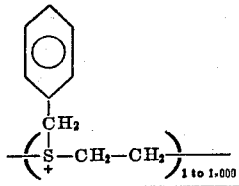
R_1	R_2	X	n	A^-
CH_3	C_3H_7		2	NO_3.
C_2H_5	C_2H_5		2	Cl.
CH_3	CH_3		2	Tosylate.
n-$C_{10}H_{21}$	n-$C_{10}H_{21}$		2	F.
CH_3	CH_3		2	Cl.
n-C_4H_9	n-C_4H_9		2	Br.
n-C_6H_{13}	n-C_6H_{13}		2	Tosylate.
C_2H_4OH	C_2H_4OH		2	F.
iso-C_4H_8OH	iso-C_4H_8OH		2	NO_3.
n-C_6H_{13}	n-C_6H_{13}		2	Br.
C_4H_9	C_2H_5	$-CH_2-CH=CH-CH_2$	2	Cl.
$CH_2=CH-CH_2$	$CH_2=CH-CH_2$	$-CH_2CH=CH-CH_2-$	2	Tolysate.
CH_3	CH_3		2	F.
CH_3	CH_3		-----	Cl.
C_2H_5	C_2H_5		-----	F.
C_2H_5	C_2H_5		-----	Cl.

TABLE I—Continued

R_1	R_2	X	n	A^-
CH_3	CH_2			NO_3
				
		n=1 to 20		
				Br

The solid electroconductive articles suitable for use in this invention may be of any size or shape and include articles formed from: metals and metal alloys, such as iron, aluminum, magnesium, zinc, lead, copper, platinum, chromium, silver and tin or a metal alloy consisting essentially of one of the aforesaid metals and the like; nonmetallic conductors, such as carbon, graphite and the like; metallic semi-conductors such as germanium, gallium and the like; organic conductors, such as electroconductive plastics and the like, and electroconductively coated substances such as plastics coated with aluminum and other like solid electroconductive materials. Metals are the preferred class of electroconductive materials, particularly lead, copper or iron alloys thereof, and chromium- or nickel-plated iron or iron alloys.

The subject invention is surprisingly operable in aqueous media on metals having a low hydrogen overvoltage, such as iron, nickel and copper, as well as on metals having a high hydrogen overvoltage, such as lead, zinc and tin. This is a tremendous advantage since (a) most of the commercial items requiring a protective or decorative coating are metals having a low hydrogen overvoltage, and (b) water is by far the preferred solvent based on availability, cost, lack of toxicity, etc.

Suitable electrolysis solvents, in addition to water, include inert organic polar solvents, such as dimethylformamide, acetonitrile, dimethylsulfoxide, hexamethylphosphoramide, tetrahydrofuran, lower alkanols, such as methanol, ethanol, isopropanol, n-butanol, and the like, and mixtures of such organic solvents, and mixtures of such organic solvents with water, and the like. The preferred solvents are those which dissolve or solvate the polysulfonium salt and are inert to the polymer coating, i.e., the solvent does not dissolve the coating to any substantial degree. Water and water-lower alkanol mixtures are therefore the preferred solvents.

The process may be suitably conducted at controlled or uncontrolled electrical potentials, as defined above; so long as sufficient electrical energy is present to attract the polysulfonium to the cathode surface and to reduce some or all of the sulfonium ions.

Since reductive coupling is essential to obtain the more useful polymer coatings from the lower molecular weight reactants, the process must be operated under conditions which maximize the reductive coupling reaction. One method of achieving this is to use the controlled-potential electrolysis, as described by L. Meites in "Technique of Organic Chemistry," A. Weissberger, editor, vol. 1, 3rd ed., p. 3281, Interscience, N.Y. (1959).

For the higher molecular weight salts, an uncontrolled potential is advantageous, i.e., the driving potential is constant and the cathode potential is uncontrolled. Polymers by their random nature and bulk are thought to physically prevent some of the attached sulfonium groups from contacting the cathode and therefore prevent complete sulfonium reduction.

To some extent, the thickness of the coating can be increased, if desired, by including an optional supporting electrolyte. Any of the conventional supporting electrolytes may be employed, such electrolytes typically being salts of strong acids, such as KCl, NaBr, Na_2SO_4, etc. Generally, a supporting electrolyte is not required and is preferably not included.

The reaction temperature may be varied from the freezing point to the boiling point of the electrolyte solution (polysulfonium salt and electrolysis solvent) so long as the applied coating is not dissolved and the sulfonium reactant is not thermally decomposed. Typically, the process is conducted at a temperature between about 20° C. and about 75° C., although higher and lower temperatures may be used. Elevated temperatures are in some instances instrumental in increasing the coating rate.

The electrolyte solution is preferably stirred, to assure a continuous supply of sulfonium ions at the cathode surface. Violent agitation which might introduce air bubbles, etc., should be avoided.

The subject process may be suitably conducted as a batch or continuous process and the cathode may be only one member or a plurality of joined members.

The process may be carried out from pH–3 to 12 but preferably from 7 to 12, basic media is preferred to reduce the problem of gassing at the electrode surface.

SPECIFIC EMBODIMENTS

The following examples further illustrate the invention:

EXAMPLE 1

Preparation and coating of poly(p-xylylene) on an aluminum cathode

p - Phenylenedimethylene - bis(dimethylsulfonium perchlorate) was prepared from the corresponding bis-(dimethylsulfonium chloride) by adding perchloric acid to an aqueous solution of the sulfonium salt. The perchlorate precipitated and was isolated by filtration.

Four grams of the perchlorate thus prepared were dissolved in 200 ml. of dimethylformamide (DMF) and placed in the cathode compartment of a three-compartment electrolysis cell. The anode and central compartments were filled DMF. An aluminum plate and a graphite rod were used as the cathode and anode, respectively. The catholyte solution was stirred during the electrolysis. The cathode potential (reducing potential) was increased until a current began to flow (~10–15 ma.) and was main-

tained at that voltage until sufficient current was passed to develop a coating on the cathode. This coating was sequentially washed with water, toluene, DMF and acetone. The white coating was scraped from the cathode and identified by infrared spectroscopy as poly(p-xylylene).

In identical experiments, except for the material used as the cathode, the following metal cathodes were similarly coated: tin, annealed steel and lead. The coated articles are resistant to oxidation in air and in water and are protected against attack by aqueous HCl. The coating in these cases was identified as poly-p-xylylene by contact infrared performed directly on the coated metals.

EXAMPLE 2

Preparation and coating of poly(p-xylylene) on an aluminum cathode

0.3 mole of xylylene dichloride, 0.62 mole of bis-(hydroxyethyl) sulfide, and 450 ml. of deionized water were placed in a stirred vessel for 5 days at 50° C. The resulting solution was diluted to 0.5 N in chloride with deionized water. The xylylene bis(diethanolsulfonium) chloride was then converted to the nitrate by adding $AgNO_3$ until no more precipitate could be detected forming in the clear supernatant solution. The supernatant liquid was then filtered to remove AgCl. Crystals of p-xylylene-bis(diethanolsulfonium nitrate) were formed when ethyl acetate and methanol were added to the water solution. The nitrate was dissolved (2 grams/80 cc. of solvent) in dimethylformamide in which the electrolysis was carried out. The catholyte solution thus prepared was placed in an open beaker cell equipped with an aluminum cathode and platinum anode.

As voltage was applied, the current moved to about 60 ma./square inch of aluminum but quickly decreased to about 20 ma./square inch. A white material coated the cathode in approximately 60 seconds. The coating was washed with acetone and water and identified by infrared analysis as poly-p-xylylene.

EXAMPLE 3

Preparation and coating of poly(p-xylylene) on a lead cathode

A 0.5 N aqueous solution of p-phenylenedimethylene-bis(dimethylsulfonium chloride) was made in KI and placed in a beaker equipped with a lead cathode and graphite anode. An electrical potential between the cathode and anode (driving potential—from constant voltage source) of about 3 volts was applied. The initial current was 50 milliamperes (ma.) which decayed to about 20 ma. in 10–20 seconds. A cloudy coating was easily seen on the cathode surface which had been machined to a shiny finish. The coating was identified as poly(p-xylylene).

EXAMPLE 4

Preparation and coating of poly(p-xylylene) on an aluminum cathode

A 0.1 N aqueous solution of p-phenylenedimethylene-bis(dimethylsulfonium chloride (and in NaOH was placed in a beaker equipped with an aluminum cathode and graphite anode. Enough current was passed to form a coating on the cathode; the coating was identified as poly(p-xylylene).

EXAMPLE 5

A polyelectrolyte prepared by polymerization of vinylbenzyldimethylsulfonium chloride was ion exchanged with Dowex 1 resin to the polysulfonium hydroxide. The viscous orange aqueous solution (ca. 5% solids by weight) was placed in a beaker equipped with a graphite anode and a steel cathode (cathode surface area was about 1 sq. in.). A potential was applied and raised to the point where 15 ma. of current was flowing. Very little hydrogen evolution (gassing) was observed. The current decayed to about 8 ma. during the 1 hour of reaction. The cathode was removed and thoroughly rinsed with water.

A blank was prepared by dipping a second steel chip into an identical polysulfonium hydroxide solution and then washing the chip with water. The blank and the test sample were dried in a hot air stream and placed in a 0.1 N aqueous NaCl solution at 80° C. for 1 hour. The blank and the uncoated portion of the test sample turned black while the coated portion of the test sample was unstained.

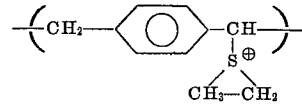
EXAMPLE 6

A polyelectrolyte was prepared by copolymerizing vinylbenzyl chloride and butyl acrylate in an aqueous emulsion, diluting the mixture to about 10% solids by weight and further reacting the copolymer with a stoichiometric excess of dimethyl sulfide to produce the corresponding polysulfonium salt (polyelectrolyte) which dissolved in the aqueous medium. More water was added to make the concentration 4% by weight.

The solution was dialyzed against deionized water until free of soluble salts and the like. The resulting solution was slightly hazy and contained 0.4% solids by weight. A portion of this solution was placed in a beaker containing a stainless steel anode and a copper wire cathode. A potential of 10 volts was applied. The initial current of 500 ma. fell immediately to less than 10 ma. The cathode was removed and washed with water. The copper wire had a thin translucent gel coating which cured when heated in air to a hard, continuous, insulating and adherent film.

EXAMPLE 7

An aqueous solution of poly(p-xylene-α-diethylsulfonium chloride) having the recurring unit

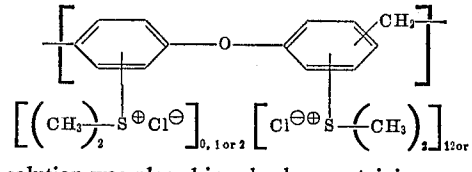


was dialyzed against deionized water until free of dissolved salts. The solution was diluted with water to 0.1% solids by weight. The solution was placed in a glass beaker containing a steel anode. (a) A steel cathode was placed in the beaker and a potential of 10 volts was applied and the current rose to 100 ma. A gel was rapidly deposited on the cathode. The cathode was removed and the coating dried (yellow coatings); (b) (a) was repeated at a higher potential and a 500 ma. initial current. A yellow coating was immediately deposited and the current decayed to less than 10 ma. The cathode was removed, washed with water and heated in air (ca. 150° C.). The resulting cured coating was a hard, continuous and insulating coating.

EXAMPLE 8

An aqueous solution (6% solids by weight) of a polyelectrolyte was prepared by reacting an excess of dimethyl sulfide with a highly branched polymer prepared from dichloromethylated diphenyl oxide; the polyelectrolyte had a wide and uneven molecular weight distribution with a major portion at about 190,000 molecular weight.

The polymer is represented by the recurring unit



The solution was placed in a beaker containing a graphite anode (a) A lead cathode was placed in the beaker and a potential was applied. The initial current of 100 ma. decayed to about 10 ma. during a 2–3 min. time interval. A good polymer coating was deposited. Similar results were obtained using a tin cathode; (b) (a) was repeated with a tin cathode except that the intial current was 500

ma. The current decayed to 200 ma. in 1 min. and good polymer coating was obtained. Similar results were obtained with a zinc cathode (current decayed to 120 ma. in 3 min.) and a light coating was obtained on an aluminum cathode.

The initial solution was diluted with dimethylformamide to 3% solids by weight and made 0.3 N in tetraethylammonium tosylate. Repeating (b) above using this solution and a copper cathode, a good coating was obtained with no substantial reduction in current.

EXAMPLE 9

An aqueous solution of a polyelectrolyte prepared by reacting an excess of dimethyl sulfide with chloromethylated polystyrene (3.5×10^{-3} moles of $Cl\ominus$/gm. of dry polymer) in water. The solution was diluted to 6% solids by weight and placed in a beaker equipped with a graphite anode and a lead cathode. A potential was applied such that an initial current of 500 ma. was achieved. The current decayed to 100 ma. in 3 min. A good coating was obtained. Similar results were achieved using a steel cathode (no substantial decay in the amperage was observed, however).

In general, the polymer coatings are useful as electrical insulators, as unusual finishes, as colored coatings and other like uses.

We claim:

1. A process for applying a polymer coating to a solid electroconductive article used as the cathode in an aqueous electrolysis system comprising an anode, a cathode, an electrolysis solvent and a means for applying and maintaining an electrical potential between said anode and cathode, said process comprising subjecting a polysulfonium salt in solution with said electrolysis solvent to an electrical potential sufficient to reduce said polysulfonium salt, said polysulfonium salt having the formula

$$[R_1R_2S\oplus]_nX\cdot nA\ominus$$

wherein R_1 and R_2 are hydrocarbon or hydroxy-substituted hydrocarbon groups of 1 to 30 carbon atoms; n is an integer and is at least 2; X is an n-valent hydrocarbon radical whose chain may be interrupted by oxygen, sulfur or nitrogen, or by a keto, ester or amide linkage; and $A\ominus$ is an electrolytically acceptable anion compatible with the solvent medium.

2. The process defined in claim 1 wherein said solvent is water.

3. The process defined in claim 1 wherein said electroconductive article is metallic.

4. The process defined in claim 3 wherein said electroconductive article is at least one of iron, copper, zinc, lead, aluminum, magnesium, chromium, silver and tin; or a metal alloy consisting essentially of one of the aforementioned metals.

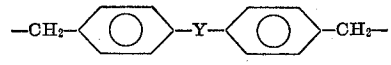
5. The process defined by claim 4 wherein said electroconductive material is lead, iron, copper or an alloy thereof.

6. The process defined by claim 1 wherein R_1 and R_2 are hydrocarbon or hydroxy-substituted hydrocarbon groups of 1 to 4 carbon atoms.

7. The process defined by claim 1 wherein n is 2 and X is $-CH_2-C_6H_4-CH_2-$,

$$-CH_2-C_6H_4-C_6H_4-CH_2-$$

or



wherein Y is alkylene, arylene or alkenylene of 1 to 10 carbon atoms, oxygen or sulfur.

8. The product produced by the process of claim 1.

9. The product produced by the process of claim 2.

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JOHN H. MACK, Primary Examiner

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U.S. Cl. X.R.

204—56 R, 59, 181

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,697,398 Dated October 10, 1972

Inventor(s) Ritchie A. Wessling and William J. Settineri

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

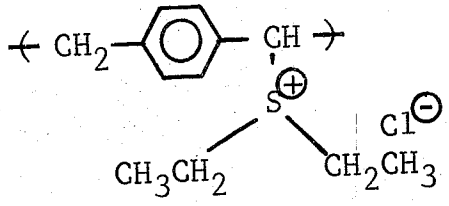
Col. 4, line 29, should read as follows:

---those of the formula $-CH_2-C_6H_4-CH_2-$, ---.

Col. 7/8, approx. line 15, delete "n=1 to 20" and insert ---n=2 to 20---.

Col. 10, line 33, delete "poly(p-xylene-α-diethylsulfo-" and insert ---poly(p-xylylene-α-diethylsulfo- ---.

Col. 10, lines 35-39, correct the formula to read as follows:



Col. 10, line 68, the last subscript of the formula now appears as "12or". Correct the subscript to read --- 1 or 2 ---.

Signed and sealed this 18th day of December 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents