(CONVENTION. By one or more persons and/or a Company.) Form 4

609297

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address (es).

x I/We (1) BASF AKTIENGESELLSCHAFT

of D-6700 Ludwigshafen, Federal Republic of Germany

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)

TIN-CONTAINING COPOLYMERS AND THEIR USE

(3) Here insert number(s) of basic application(s)

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered (3)

P38 17 069.8

(4) Here insert Name of basic Country or Countries, and basic date or dates

for a patent or similar protection made in (4) Federal Republic of Germany on 19th May 1988

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 30·1·91.

x~~My~~/Our address for service is Watermark Patent & Trademark Attorneys, ~~Messrs Baldwin Waters & Sons Patent Attorneys~~, 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 17th day of May 1989

(5) Signature (s) of Applicant (s) or Seal of Company Signatures of its Officers as prescribed by its Articles of Association

(5) BASF AKTIENGESELLSCHAFT

009115 180589 by

Louis C. Gebhardt

Registered Patent Attorney

O.Z. 0050/39930

(CONVENTION. Company.) Form 8

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1962

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

(1) Here insert (in full) Name of Company.

In support of the Convention Application made by(1) BASF Aktiengesellschaft, a German Joint Stock Company of D-6700 Ludwigshafen, Federal Republic of Germany;

(hereinafter referred to as the applicant) for a Patent

(2) Here insert title of Invention.

for an invention entitled:(2) Tin-containing copolymers and their use

(3) Here insert full Name and Address, of Company official authorised to make declaration.

(3) We, Dr. PETER RICHTERS and PETER BARZ, citizens of the Federal Republic of Germany, residing, respectively, at 40 Kerschensteinerstrasse, D-6700 Ludwigshafen; and 20 Hochfeldstrasse, D-6700 Ludwigshafen; Federal Republic of Germany;

do solemnly and sincerely declare as follows:

1. ~~I am~~ We are authorised by the applicant for the patent to make this declaration on its behalf.

(4) Here insert basic Country or Countries followed by date or dates and basic Applicant or Applicants.

2. The basic application as defined by Section 141 of the Act was made in(4) the Federal Republic of Germany under No. P 38 17 069.8 on the 19th day of May 19 88, by BASF Aktiengesellschaft

~~on the day of 19 by~~

(5) Here insert (in full) Name and Address of Actual Inventor or Inventors.

3. (5) KASPAR BOTT, GREGOR LEY, ECKEHARDT WISTUBA, citizens of the Federal Republic of Germany, residing, respectively, at 57 Wenderstrasse, 6800 Mannheim 1; In den Trankstuecken, 6719 Wattenheim; 7 Im Obergarten, 6702 Bad Duerkheim; Federal Republic of Germany;

~~is~~/are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of KASPAR BOTT, GREGOR LEY and ECKEHARDT WISTUBA

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at D-6700 Ludwigshafen, Federal Republic of Germany

this 25th day of April 19 89

(12) PATENT ABRIDGMENT (11) Document No. AU-B-34936/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 609297

(54) Title
TIN-CONTAINING COPOLYMERS AND THEIR USE

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BASF AKTIENGESELLSCHAFT

(72) Inventor(s)
KASPAR BOTT; GREGOR LEY; ECKEHARDT WISTUBA

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS, Locked Bag 5, HAWTHORN VIC 3122

(57) The present invention relates to copolymers which contain organically bonded tin, in the form of aqueous dispersions, and their use as biocidal binders for wood-protecting glazes, emulsion paints and resin-bonded renders.

CLAIM

9. A polymer as claimed in claim 1, which contains carbonyl-containing monomers as herein defined copolymerized as monomers of group (e).

609297

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

Class Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :

This document contains the amendments made under Section 49 and is correct for printing

Name of Applicant : BASF AKTIENGESELLSCHAFT

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Actual Inventor: KASPAR BOTT, GREGOR LEY and ECKEHARDT WISTUBA

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50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

TIN-CONTAINING COPOLYMERS AND THEIR USE

The following statement is a full description of this invention, including the best method of performing it known to :- us

Tin-containing copolymers and their use

The present invention relates to copolymers which contain organically bonded tin, in the form of aqueous dispersions, and their use as biocidal binders for wood-protecting glazes, emulsion paints and resin-bonded renders.

Polymers containing organically bonded tin are familiar as binders for antifouling paints, ie. for paints used for protecting ships' hulls, buoys and other objects which come into contact with sea water from becoming covered with a growth of slime-forming bacteria, algae, mussels and other sea creatures. It has been found that polymers of this type must fulfil two conditions in order to be suitable for this purpose: 1) they must contain substantial amounts of organically bonded tin as copolymerized units or, alternatively, must be mixed with substances which are soluble in sea water and contain tin or other toxic components, and 2) they must undergo slow hydrolysis in a controllable manner when they come into contact with sea water and must go into solution in order to be able to exhibit their biocidal action (cf. M.H. Gitlitz, Journal of Coatings Technology, 53 (1981), No. 678, 46-52, in particular 50; U.S. Patents 4,021,392 and 4,532,269; British Patent Application 20 87 415 and European Patent Application 151 809).

Biocidal activity is also desirable in the case of wood-protecting glazes, emulsion paints and resin-bonded renders. This has been achieved to date by mixing miocidal substances into the stated products. Although this gives satisfactory effects, ecological problems arise since the biocidal active ingredients as such are, as a rule, hazardous to health and can therefore only be introduced into the products if appropriate safety precautions are adhered to, and since they may migrate out of their layers after the products have been processed. Furthermore, attempts to use the tin-containing polymers,

which have proven useful for antifouling paints, for wood-protecting glazes, emulsion paints and resin-bonded renders do not give satisfactory results since the easy hydrolyzability and the high tin content make them toxicologically unacceptable and they often do not give sufficiently stable coatings.

We have found tin-containing copolymers in the form of aqueous dispersions which, when used as biocidal binders for wood-protecting glazes, emulsion paints and resin-bonded renders, do not have the disadvantages described and, despite a very low content of organically bonded tin and high stability to hydrolysis, display a very good biocidal action which is evident in particular from the pronounced inhibition of growth of fungi, algae, lichen, mosses and the like. Nevertheless, they themselves cannot be regarded as toxic to sensitive fish, such as the rainbow trout.

The novel copolymers are in the form of an aqueous dispersion; they contain

(a) from 0.03 to 2% by weight of tin in the form of units of organotin compounds having one or more polymerizable C=C bonds,

(b) from 10 to 80% by weight of units of rigidity-imparting monomers,

(c) from 90 to 20% by weight of units of plasticizing monomers,

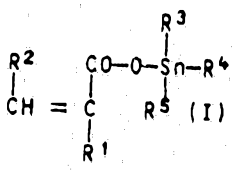
(d) from 0 to 5% by weight of units of acrylic acid, methacrylic acid, vinylsulfonic acid, maleic acid, acrylamide, methacrylamide or acrylamide or methacrylamide which is substituted at the nitrogen atom by C_1-C_8-alkyl, hydroxymethyl or C_1-C_8-alkoxymethyl, and

(e) from 0 to 5% by weight of other monomers which neither impart hydrophilic properties nor are readily hydrolyzable,

the percentages being based on anhydrous polymer, and

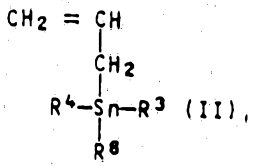
they have a glass transition temperature of from -40 to +50°C, preferably from -20 to +30°C.

Suitable organotin compounds which are incorporated into the novel polymers are in principle all those which contain one or more polymerizable C=C bonds, preferably one or two such bonds. Because they are easily obtainable, organotin compounds having one or two acrylic acid, methacrylic acid, maleic acid, itaconic acid or allyl radicals are preferred. Of particular interest are the substances of the general formulae



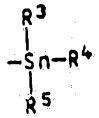
(I)

and

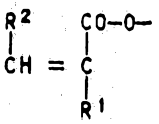


(II),

where R^1 is hydrogen or a group of the formula $-CH_2-X$, R^2 is a group of the formula -X, X is hydrogen or a radical of the formula -CO-O-A (and where two radicals X are present at least one is hydrogen), A is hydrogen, C_1-C_8-alkyl or a group of the formula



R^3 and R^4 are identical or different C_1-C_8-alkyl groups, cycloalkyl groups or phenyl groups, R^5 is a group of the type stated for R^3 and R^4 or a group of the formula



and R^6 is a group of the type stated for R^3 and R^4 or allyl.

The organotin compounds of the stated formulae are known or are obtainable by known processes. Examples of such compounds are: tri-n-butyltin acrylate, tri-n-

butyltin methacrylate, tricyclohexyltin methacrylate, tricyclohexyltin acrylate, triphenyltin acrylate, triphenyltin methacrylate, tri-n-propyltin acrylate, tri-n-propyltin methacrylate, triisopropyltin acrylate, triisopropyltin methacrylate, tri-sec-butyltin acrylate, tri-sec-butyltin methacrylate, triethyltin acrylate, triethyltin methacrylate, diethylbutyltin acrylate, diethylbutyltin methacrylate, diethylamyltin acrylate, diethylamyltin methacrylate, diamylmethyltin acrylate, diamylmethyltin methacrylate, propylbutylamyltin acrylate, propylbutylamyltin methacrylate, diethylphenyltin acrylate, diethylphenyltin methacrylate, ethyldiphenyltin acrylate, ethyldiphenyltin methacrylate, n-octyldiphenyltin acrylate, n-octyldiphenyltin methacrylate, diethyloctyltin acrylate, diethyloctyltin methacrylate, di-n-butyltin diacrylate, di-n-butyltin dimethacrylate, mono- and di-(tripropyltin) maleate, mono- and di-(tricyclohexyltin) maleate, mono- and di-(triphenyltin) maleate, mono- and di-(tri-n-butyltin) maleate and the corresponding mono- and diesters of itaconic and citraconic acid, allyltri-n-butyltin, diallyldi-n-butyltin, allyltricyclohexyltin, diallyldicyclohexyltin, allyltriphenyltin and diallyldiphenyltin. Because of their particularly good activity, the substances of the formulae (I) and (II) which are preferred are those whose radicals R^3, R^4, R^5 and R^6 are each C_3-C_6-alkyl, phenyl or cyclohexyl, those whose radicals R^3, R^4 and R^5 or R^3, R^4 and R^6 are identical having the advantage of being particularly readily obtainable and therefore being preferred.

The organotin compounds (a) are copolymerized with their C=C double bond or bonds in the polymers of the novel dispersions in an amount such that the polymers contain from 0.03 to 2, preferably from 0.3 to 1.5, % by weight of tin.

The polymers of the invention furthermore contain rigidifying and plasticizing monomers as copolymerized

units. The term rigidifying or plasticizing denotes monomers which are sometimes referred to inaccurately in the literature as rigid or flexible, ie. monomers which, when polymerized by themselves, give rigid or flexible homopolymers. In this sense, rigidifying monomers are in general those whose homopolymers have glass transition temperatures of from about 25 to 120°C, while plasticizing monomers are in general those whose homopolymers have glass transition temperatures of from about -60 to +25°C. Although it is known that there are fluid transitions between these groups of monomers, typical members are known for both groups.

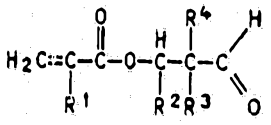
Typical rigidifying monomers (b) are, for example, styrene, methyl methacrylate, tert-butyl acrylate, acrylonitrile, vinyl acetate, vinylidene chloride and vinyl chloride. Of these, methyl methacrylate and styrene are preferred for the purpose of the present invention.

Typical plasticizing monomers (c) are, for example, acrylates and methacrylates of nontertiary alkanols of 2 to 8 carbon atoms, butadiene and vinyl propionate. For the purposes of the present invention, acrylates and methacrylates of nontertiary alkanols of 2 to 8 carbon atoms are preferred among these.

In addition to the stated groups of monomers, the polymers of the invention may contain, as copolymerized units, minor amounts, ie. not more than 7, preferably not more than 3.5, % by weight, of monomers from the following group (d): acrylic acid, methacrylic acid, vinylsulfonic acid, maleic acid (these acids in free form or in the form of their salts, in particular the alkali metal and ammonium salts), acrylamide and methacrylamide and their derivatives substituted at the nitrogen atom by C_1-C_8-alkyl, hydroxymethyl or C_1-C_8-alkoxymethyl, such as N-methylacrylamide, N-isobutylacrylamide, N-ethoxy- or N-butoxymethylacrylamide, and hydroxyalkyl acrylates and

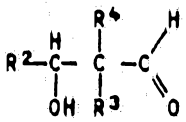
methacrylates, such as hydroxyethyl acrylate and 2-hydroxy- and 3-hydroxypropyl acrylate.

Finally, the novel polymers may contain up to 5% by weight of other monomers (e), provided that they neither impart hydrophilic properties nor are readily hydrolyzable, since they could otherwise adversely affect the advantageous properties of the polymers. Among these monomers of group (e), particularly noteworthy ones are those which are capable of crosslinking the polymers by chemical reactions, for example monomers containing epoxy groups, such as glycidyl acrylate and glycidyl methacrylate. Other interesting monomers of group (e) are those which have carbonyl groups. For the purposes of the present invention, carbonyl-containing monomers are not, for example, esters, such as ethyl acrylate or vinyl acrylate, or amides, such as acrylamide, or carboxylic acids, such as acrylic acid, but monomers having one or more aldo or keto groups and a polymerizable double bond. Of particular interest are acrolein, diacetoneacrylamide, formylstyrene, vinyl alkyl ketones of, preferably, 4 to 7 carbon atoms, in particular vinyl methyl ketone, vinyl ethyl ketone and vinyl isobutyl ketone, and/or (meth)-acryloyloxyalkylpropanals of the general formula (III)



(III)

where R^1 is -H or $-CH_3$, R^2 is -H or alkyl of 1 to 3 carbon atoms, R^3 is alkyl of 1 to 3 carbon atoms and R^4 is alkyl of 1 to 4 carbon atoms. Such (meth)acryloyloxyalkylpropanals can be prepared by the process described in German Patent Application P 27 22 097.9, by esterification of ß-hydroxyalkylpropanals of the general formula (IV)



(IV)

where R^2, R^3 and R^4 have the meanings stated for the general formula (III), in the presence of inert diluents and small amounts of sulfonic acids and mineral acids at from 40 to 120°C, in particular from 60 to 90°C. Other keto-containing monomers are diacetone acrylate, acetonyl acrylate, diacetone (meth)acrylate, diacetoneacrylamide, diacetonemethacrylamide, 2-hydroxypropyl acrylate acetylacetate and butane-1,4-diol acrylate acetylacetate. The amount of copolymerized carbonyl-containing or keto-containing comonomers is preferably from 1 to 5% by weight, based on the copolymers. The aqueous dispersions of the novel copolymers can be prepared in a conventional manner by copolymerization of the monomers in aqueous emulsion using the conventional emulsifiers and dispersants, and generally have a copolymer concentration of from 40 to 60% by weight. They contain, as emulsifiers and dispersants, in general from 0.2 to 3% by weight, based on the amount of copolymer, of anionic and/or non-ionic emulsifiers, such as sodium dialkylsulfosuccinates, sodium salts of alkylsulfonic acids, sodium, potassium and ammonium alkylsulfates, alkali metal salts of sulfonic acids, alkali metal salts of oxyalkylatedfatty C_{12}-C_{24}-alcohols and of oxyalkylated alkylphenols, as well as oxyethylated fatty acids, fatty alcohols and/or fatty amides, oxyethylated alkylphenols, and sodium salts of fatty acids, such as sodium stearate and sodium oleate. The ratios of the monomers, in particular those from groups (b) and (c), are chosen within the stated limits in such a way that the polymers have a glass transition temperature of from -40 to +50°C, preferably from -20 to +30°C. The glass transition temperature is determined by

a conventional method, for example from the measurement of the modulus of elasticity in the creep test as a function of temperature or by differential thermal analysis (DTA) (cf. A. Zosel, Farbe Lack 82 (1976), 125-134). The mean molecular weight of the novel copolymers, determined using an ultracentrifuge, is in the range usual for film forming polymers, ie. more than 20,000, preferably more than 50,000. Of particular importance with regard to applications technology are novel copolymers which have a mean molecular weight of more than 100,000. The particle sizes of the dispersions, determined by dynamic light scattering in a Nanosizer from Coulter Electronics, are in general from 50 to 500 nm, or from 80 to 280 nm in the case of preferred dispersions of the novel copolymers.

If the polymers of the invention contain, as copolymerized units, monomers possessing epoxy or carbonyl groups, they can react with water-soluble aliphatic dihydrazine compounds by crosslinking. Such dihydrazine compounds can be added directly to the dispersions of the polymers, advantageously in an amount of from 0.05 to 1, preferably from 0.4 to 0.6, mole per mole of the epoxy or carbonyl groups present in the polymers. Particularly suitable dihydrazine compounds are dihydrazides of aliphatic dicarboxylic acids of 2 to 10, in particular 4 to 6, carbon atoms, such as oxalic acid dihydrazide, malonic acid dihydrazide, succinic acid dihydrazide, glutaric acid dihydrazide, adipic acid dihydrazide, sebacic acid dihydrazide, maleic acid dihydrazide, fumaric acid dihydrazide and/or itaconic acid dihydrazide. Other suitable substances are water-soluble aliphatic dihydrazines of 2 to 4 carbon atoms, such as ethylene-1,2-dihydrazine, propylene-1,3-dihydrazine and butylene-1,4-dihydrazine.

It has proven particularly useful if, in addition to the dihydrazine compounds, water-soluble heavy metal salts are added to the dispersions of the novel copoly-

mers in a conventional manner in an amount of from 0.0002 to 0.02, in particular from 0.002 to 0.01, mole per mole of dihydrazine compound. The heavy metal salts may be, for example, those of manganese, cobalt, nickel, iron, copper, chromium, lead or vanadium. The acetates, sulfates, nitrates and nitrites are particularly suitable. Although the chlorides can also be used, they sometimes have undesirable side effects.

The aqueous dispersions of the novel polymers are very suitable as biocidal binders for wood-protecting glazes, emulsion paints and resin-bonded renders. In an unpigmented form which may be diluted with water, they are suitable, for example, as primers. For the preparation of pigmented coating materials, the usual pigments and pigment formulations can be used in the conventional amounts. Titanium dioxide (rutile) as well as white lead, lithopone and colored pigment formulations are particularly suitable. Examples of suitable fillers for the coating materials are chalk, calcite, talc and fine sand, in the conventional amounts. In general, ionic and/or nonionic dispersants, for example low molecular weight polyacrylic acids or oxyethylated p-nonylphenol, thickeners, such as cellulose ethers, polyurethane thickeners, styrene/maleic acid copolymers and/or polyvinylpyrrolidone, film forming assistants, such as glycol ethers, glycol ether acetates, pine oil or alcohols of 8 to 15 carbon atoms and 1 to 3 OH groups which are liquid at room temperature, and/or leveling agents, such as alkyl polyethylene glycol ether bisurethanes, can also be used for the coating materials. If necessary, preservatives, such as chloroacetamide or chlorophenols, may also be used, although this is generally not necessary.

The novel polymers are also suitable as binders for resin-bonded renders and stone-chip renders and can be used for this purpose in the conventional amounts. The renders contain in general from 5 to 12% of binder

(solid) based on copolymers whose minimum film forming temperature (= MFT) is usually from 5 to 30°C, and, in addition to the mineral components, such as pigments (eg. titanium white), fillers (eg. chalk, talc, etc.) and granules based on calcium carbonate and/or silica, which have particle sizes of about 0.5-4 mm depending on the type and structure of the render, also thickeners, such as cellulose ethers, salts of high molecular weight polyacrylic acids, and/or polyvinylpyrrolidone, and film forming assistants which permit a film forming temperature of ≤ 5°C. The film forming assistants used are esters of higher fatty acids, eg. diisopropyl adipate, and aromatics-containing gasolines, glycol ethers, glycol ether acetates and mixtures of these. Stone-chip renders contain as mineral components only granules, and no fillers.

The dispersions of the novel polymers have such a good biocidal activity that they themselves as well as the coating materials prepared from them have a long shelf life without the danger of attack by microorganisms. It is therefore generally not necessary to add additional preservatives to them. This is demonstrated by the pot preservation test described at the end of the Examples.

The abbreviations used in the Examples below have the following meanings:
MMA = methyl methacrylate; nBA = n-butyl acrylate; AM = acrylamide; MAM = methacrylamide; AA = acrylic acid; S = styrene; iBA = isobutyl acrylate; GMA = glycidyl methacrylate; nBMA = n-butyl methacrylate. Parts and percentages are by weight.

[EXAMPLE 1]

The following are initially taken in a Witt pot equipped with a thermostat, an anchor stirrer, a reflux condenser, various feed vessels, a thermometer and a nitrogen inlet:

350 parts of fully demineralized water and
4.5 parts of a 35% strength aqueous solution of the Na salt of an acidic sulfuric ester of an adduct of 1 mole of nonylphenol and 25 moles of ethylene oxide.

The initially taken mixture is flushed with nitrogen and heated to 90°C. Thereafter, 6 parts of an aqueous solution of 2.5 parts of Na peroxydisulfate in 60 parts of fully demineralized water are added, and the remainder of the solution is then added uniformly to the reactor in the course of 3.5 hours, as feed I. At the same time, a start is made with the introduction of feed II, which consists of an emulsion of
168 parts of fully demineralized water,
22 parts of the abovementioned emulsifier solution,
294 parts of MMA,
284 parts of nBA,
31 parts of tri-n-butyltin methacrylate,
9 parts of AM and
9 parts of AA,
the said emulsion being added uniformly to the reactor in the course of 3 hours. Polymerization is continued for a further 1.5 hours at the same temperature, the dispersion is cooled and the pH is brought to 8-10 with ammonia water. A pale yellow dispersion which has moderate viscosity, a solids content of about 49% by weight and a mean particle size (measured in the Nanosizer) of about 150 nm is obtained, which, when spread on glass and dried, gives a clear glossy film. It contains 1.5% of tin, based on dry polymer.

[EXAMPLE 2]

The procedure described in Example 1 is followed, except that
288 parts of S,
280 parts of nBA,
31 parts of tri-n-butyltin methacrylate,
9 parts of AM and

9 parts of AA
are used as monomers in feed II. A pale yellowish dispersion which has moderate viscosity, a solids content of about 48% by weight and a mean particle size (Nanosizer) of about 130 nm is obtained. It contains 1.6% of tin, based on dry polymer.

[EXAMPLE 3]

The procedure described in Example 1 is followed, except that a mixture of
304 parts of MMA,
294 parts of nBA,
12.5 parts of tri-n-butyltin methacrylate,
7 parts of MAM and
6 parts of AA
is used in feed II.

A virtually colorless dispersion having a solids content of about 50% by weight and a mean particle size (Nanosizer) of about 160 nm is obtained. It contains 0.6% of tin, based on dry polymer.

[EXAMPLE 4]

The procedure described in Example 1 is followed, except that a mixture of
165 parts of S,
145 parts of MMA,
292 parts of nBA,
12.5 parts of tri-n-butyltin methacrylate,
2.5 parts of AM and
4 parts of methacrylic acid
is used in feed II.

A virtually colorless dispersion having a solids content of about 48% by weight and a mean particle size (Nanosizer) of about 120 nm is obtained. It contains 0.6% of tin, based on dry polymer.

[EXAMPLE 5]

The procedure described in Example 4 is followed, except that 12.5 parts of diallyldi-n-butyltin is used

instead of tri-n-butyltin methacrylate.

A virtually colorless dispersion having a solids content of about 50% by weight and a mean particle size (Nanosizer) of about 180 nm is obtained. It contains 0.76% of tin, based on dry polymer.

[EXAMPLE 6]

The procedure described in Example 4 is followed, except that, instead of tri-n-butyltin methacrylate, 12.5 parts of di-n-butyltin dimethacrylate are used and are added to the last third of feed II.

A virtually colorless dispersion having a solids content of about 50% by weight and a mean particle size (Nanosizer) of about 140 nm is obtained. It contains 0.59% of tin, based on dry polymer.

[EXAMPLE 7]

An apparatus as described in Example 1 is used, except that it has a further feed vessel. A mixture of
700 parts of fully demineralized water and
1.5 parts of a freshly prepared 1% strength iron(II) sulfate solution
is initially taken.

A solution of
11.5 parts of potassium peroxydisulfate in
365 parts of fully demineralized water
is used as feed I.

Feed II consists of
365 parts of fully demineralized water,
25 parts of the 35% strength solution of the emulsifier from Example 1,
15 parts of a 40% strength solution of the Na salt of a C_{14}-C_{18}-alkylsulfonate,
650 parts of MMA,
750 parts of iBA,
75 parts of diacetoneacrylamide and
30 parts of tri-n-butyltin methacrylate.

Feed III is composed of

100 parts of fully demineralized water,
15 parts of the solution of the emulsifier from Example 1,
7.5 parts of the solution of the abovementioned alkylsulfonate and
2 parts of sodium sulfoxylate.

The initially taken mixture flushed with N_2 is heated to 40°C, 5% by weight of feed I and 5% by weight of feed II are added and the emulsion polymerization is initiated by adding 5% of feed III all at once. After 15 minutes, a start is made with the introduction of feeds I, II and III, which are added uniformly in the course of 2 1/2, 2 and 3 hours, the internal temperature being kept at about 50°C. Thereafter, the mixture is heated at 85°C for about 1 hour and then cooled to room temperature and brought to pH 7-8 with ammonia water, and 30 parts of adipic acid dihydrazide are also stirred into the dispersion.

A virtually colorless dispersion having a mean particle diameter (Nanosizer) of about 190 nm and a solids content of about 46% by weight is obtained. It contains 0.6% of tin, based on dry polymer.

[EXAMPLE 8]

An apparatus as described in Example 1 is used, except that
1,020 parts of fully demineralized water
are initially taken,
500 parts of demineralized water,
72 parts of the solution of the emulsifier from Example 1,
975 parts of nBA,
225 parts of GMA,
225 parts of nBMA,
75 parts of diacetoneacrylamide and
50 parts of tri-n-butyltin methacrylate
are employed as feed I and

a solution of
7.5 parts of sodium peroxydisulfate in
250 parts of fully demineralized water
is used as feed II.

The initially taken mixture flushed with N_2 is heated to 85°C. 3% of feed I and 3% of feed II are then added. After a further 15 minutes, a start is made with the introduction of feeds I and II, which are added uniformly and concurrently to the reactor in the course of 2 hours. Polymerization is continued for 1 hour, after which the mixture is cooled to room temperature and 45 parts of adipic acid dihydrazide are also stirred into the dispersion.

A virtually colorless dispersion having a solids content of about 46% by weight, a pH of about 4 and a mean particle size (Nanosizer) of about 390 nm is obtained. It contains 1% of tin, based on dry polymer.

[EXAMPLE 9]

The procedure described in Example 1 is followed, except that, instead of 31 parts, only 12 parts of tri-n-butyltin methacrylate are used in feed II. The dispersion obtained corresponds to that of Example 1, except that it contains only 0.6% of tin, based on dry polymer.

[EXAMPLE 10]

The procedure described in Example 2 is followed, except that, instead of 31 parts, only 12 parts of tri-n-butyltin methacrylate are used in feed II. The resulting dispersion corresponds to that of Example 2, except that it contains only 0.6% of tin, based on dry polymer.

[EXAMPLE 11]

From the polymer dispersion according to Example 9 and from a tin-free polymer dispersion prepared by the method of Example 1, omitting the tri-n-butyltin methacrylate, a wood-protecting glaze was in each case prepared according to the following formulation:

	A according to the invention	B Comparison
Water	100 parts	100 parts
Ammonium polyacrylate, 30% strength in water	2 parts	2 parts
Propylene glycol	50 parts	50 parts
Flatting agent (SiO_2)	17 parts	17 parts
Fungicide/algicide [1]	-	15 parts
Transparent aqueous iron oxide paste	70 parts	70 parts
Polymer dispersion according to Example 9	720 parts	-
Polymer dispersion, tin-free	-	720 parts
Butylglycol	24 parts	24 parts
Antifoam based on mineral oil	2 parts	2 parts

[1] Commercial product for fungicidal and algicidal treatment of wood coating materials, designated as toxic to fish by the manufacturer.

The two wood-protecting glazes were applied to pine boards in an amount of 150 g/m^2, and the boards were exposed to the weather in the open in a 45° position for 1 1/2 years. After this time, the sample which had been treated with glaze A and did not contain any components toxic to fish was just as free of infestation by algae and fungi as the comparative sample according to the prior art.

EXAMPLES 12 AND 13

From the polymer dispersions according to Examples 9 and 10 and from tin-free polymer dispersions prepared by the methods of Examples 1 and 2, omitting the tri-n-butyltin methacrylate, masonry paints were prepared according to the formulations below. The formulations of Examples 12 and 13 each contain a novel polymer dispersion, while those of Comparative Examples 12a and b and 13a and b each contain a corresponding, but tin-free,

polymer dispersion, the Comparative Examples denoted by a relating to formulations free of fungicide/algicide and those denoted by b relating to formulations to which a commercial fungicide and algicide has been added.

The masonry paints were applied to pine boards in an amount of 300 g/m^2 and exposed to the weather in the open for one year. After this time, the coated front surface of all samples showed no growth; the back exhibited the different levels of growth indicated at the end of the Table.

	Examples					
	12	12a	12b	13	13a	13b
Water	77	77	77	77	77	77
Ammonium polyacrylate, 30% strength in water	2	2	2	2	2	2
Sodium polyphosphate, 10% strength in water	10	10	10	10	10	10
Concentrated ammonia	2	2	2	2	2	2
Commercial fungicide and algicide	-	-	7.4	-	-	7.4
Mineral spirit 180/220°C	12	12	12	12	12	12
Mixture of butyl glutarate, adipate and succinate	12	12	12	12	12	12
Hydroxyethylcellulose, 2% strength in water	110	110	110	110	110	110
Polyurethane thickener, 5%	5	5	5	5	5	5
Titanium white	150	150	150	150	150	150
Chalk	180	180	180	180	180	180
Talc	60	60	60	60	60	60
Silicone-based antifoam	2	2	2	2	2	2
Polymer dispersion according to Example 9	375	-	-	-	-	-
Polymer dispersion according to Example 1 but tin-free	-	375	375	-	-	-
Polymer dispersion according to Example 10	-	-	-	375	-	-
Polymer dispersion according to Example 2 but tin free	-	-	-	-	375	375
Growth on the back after exposure to weather in the open for 1 year	slight pronounced		moderate	none	moderate	slight

EXAMPLES 14 AND 15

From the polymer dispersions according to Examples 9 and 10 and from tin-free polymer dispersions prepared by the methods of Examples 1 and 2, omitting the tri-n-butyltin methacrylate, resin-bonded renders were prepared according to the formulations below. The formulations of Examples 14 and 15 each contain a novel polymer dispersion, while those of Comparative Examples 14a and 15a each contain a corresponding, but tin-free, polymer dispersion but also a commercial fungicide and algicide.

The renders were applied to fiber cement boards in an amount of 3,000 g/m^2 and exposed to the weather in the open in a 45° position for one year. After this time, all render surfaces were free of growth.

	Example			
	14	14a	15	15a
Polymer dispersion according to Example 9	170	-	-	-
Polymer dispersion according to Example 1, but tin-free	-	170	-	-
Polymer dispersion according to Example 10	-	-	170	-
Polymer dispersion according to Example 2, but tin-free	-	-	-	170
Hydroxyethylcellulose, 3% strength in water	21	21	21	21
Tripotassium phosphate, 50% strength in water	5	5	5	5
Polyethylene wax dispersion, 65% strength in water	3	3	3	3
Silicone-based antifoam	4	4	4	4
Commercial fungicide and algicide	-	3.4	-	3.4
Mineral spirit 180/220°C	20	20	20	20
Dibutyl adipate	20	20	20	20
Titanium white	32	32	32	32
Chalk	344	344	344	344
Aluminum silicate	79	79	79	79
Calcium carbonate granules 1.5 mm	300	300	300	300

Pot preservation test

The coating materials described in Examples 11A, 11B, 12, 12b, 13, 13b, 14, 14a, 15 and 15a were tested for their shelf life as follows:

The coating materials were inoculated with a mixture of the following bacteria, yeasts and molds:

Pseudo. aeruginosa	Candida boidinii
Citrobac. freundii	Geotrichum candidum
Proteus vulgaris	
E. coli	Aspergillus niger
Klebsiella pneum.	Pen. funiculosum
Pichia bispora	

Candida lipolytica

The inoculated mixtures were then stored at 30°C in closed vessels. After storage for 7 days and 21 days, samples were taken and transferred to a nutrient medium in order to evaluate the susceptibility of the coating materials by observing the development of microorganisms.

Result: Like the prior art mixtures containing fungicide and algicide, the coating materials containing the novel polymers showed no infestation by microorganisms, although they were free of preservatives.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A tin-containing polymer of ethylenically unsaturated monomers in the form of an aqueous dispersion, which contains, as copolymerized units,

(a) from 0.03 to 2% by weight of tin in the form of units of organotin compounds having one or more polymerizable C=C bonds,

(b) from 10 to 80% by weight of units of rigidity-imparting monomers,

(c) from 90 to 20% by weight of units of plasticizing monomers,

(d) from 0 to 7% by weight of units of acrylic acid, methacrylic acid, vinylsulfonic acid, maleic acid, acrylamide, methacrylamide or acrylamide or methacrylamide which is substituted at the nitrogen atom by C_1-C_8-alkyl, hydroxymethyl or C_1-C_8-alkoxymethyl, and

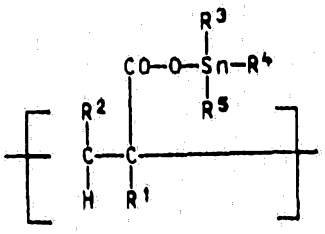
(e) from 0 to 5% by weight of other monomers which neither impart hydrophilic properties nor are readily hydrolyzable,

the percentages being based on dry polymer, and has a glass transition temperature of from -40 to +50°C.

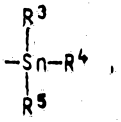
2. A polymer as claimed in claim 1, which contains from 0.3 to 1% by weight, based on anhydrous polymer, of tin.

3. A polymer as claimed in claim 1, which has a glass transition temperature of from -20 to +30°C.

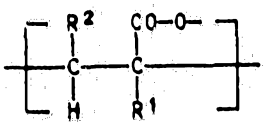
4. A polymer as claimed in claim 1, which contains the tin in the form of units of the formula



where R^1 is hydrogen or a group of the formula $-CH_2-X$, R^2 is a group of the formula -X, both radicals X are hydrogen or one radical X is hydrogen and the other is a group of the formula -CO-O-A, A is hydrogen, C_1-C_8-alkyl or a group of the formula



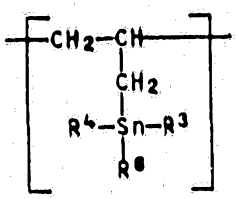
R^3 and R^4 are identical or different C_1-C_8-alkyl groups, cycloalkyl groups or phenyl groups, and R^5 is a group of the type stated for R^3 and R^4 or a group of the formula



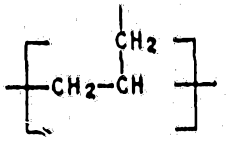
5. A polymer as claimed in claim 4, which contains the tin in the form of units of tri-n-butyltin acrylate or methacrylate.

6. A polymer as claimed in claim 4, which contains the tin in the form of units of di-n-butyltin diacrylate or dimethacrylate.

7. A polymer as claimed in claim 1, which contains the tin in the form of units of the formula



where R^3 and R^4 are identical or different C_1-C_8-alkyl groups, cycloalkyl groups or phenyl groups and R^6 is a group of the type stated for R^3 and R^4 or a group of the formula



8. A polymer as claimed in claim 7, which contains the tin in the form of units of diallyldi-n-butyltin or of diallyldicyclohexyltin.

9. A polymer as claimed in claim 1, which contains carbonyl-containing monomers as herein defined copolymerized as monomers of group (e).

10. A polymer as claimed in claim 9, which is in the form of an aqueous dispersion which contains one or more dihydrazine compounds in an amount of from 0.05 to 1 mole per mole of carbonyl groups.

11. A polymer as claimed in claim 10, which is in the form of an aqueous dispersion which contains one or more water-soluble heavy metal salts in an amount of from 0.0002 to 0.02 mole per mole of dihydrazine compound.

DATED this 17th day of May 1989.

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