

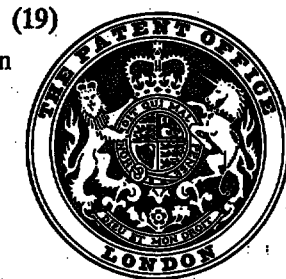
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(54) TERPOLYMERS OF MALEIC ANHYDRIDE AND THEIR USE AS SCALE CONTROL AGENTS

(71) We, PFIZER INC., a Corporation organised under the laws of the State of Delaware, United States of America, of 235 East 42nd Street, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

Acute shortage of potable water in some areas of the world is a problem for which sea water is seen as an answer. Conversion of it to fresh water by various desalination processes, however, is plagued by a technological problem resulting from the nature of the inorganic salts contained in the sea water.

They have low aqueous solubility and their precipitates can hinder the mechanism or manner of the particular desalination process used, examples of such effects being the blockage of semipermeable membranes of an osmotic process and the reduction of heat transfer of a distillation process. This will lower the efficiency of the desalination and ultimately cause such deterioration of performance that the desalination process must be stopped and the apparatus cleaned or replaced.

These salt precipitates are commonly known as scale and scale control research has been based upon the use of chemical agents, usually polymers, to control scale deposition although some have included surfactants. A common use-trait of most control agents is the very low ratio of agent to inorganic salt necessary to contain a retard precipitation. Thus, it is inferrable that the control effect is caused by complexation at the crystal growth site which repels incoming nuclei and not chelation of the inorganic cations of the salt.

The most common polymers selected for use as scale control agents are polymethacrylic acid, polyacrylic acid and polymaleic acid and their copolymers with monomers such as acrylamide and vinyl acetate. Some of the more recently developed scale control polymers are Hydrolyzed Polymaleic Anhydride (U.S. 3,810,832); Maleic Anhydride-Vinyl Acetate Copolymer (U.S. 3,715,307); Hydrolyzed Copolymer of Maleic Anhydride and Monoethylenically Unsaturated Monomer of Mixtures Thereof (GB 1414918); Maleic Anhydride Copolymers and Terpolymers (Dutch Patent Application O.I.N. 7506874); Acrylic Acid Polymers (U.S. 3,514,376); Methacrylic Acid Polymer (U.S. 3,444,054); Maleic Acid Copolymers (U.S. 3,617,577); Styrene-Maleic Anhydride Copolymers (U.S. 3,289,734); and Polyacrylic Acid (U.S. 3,293,152).

A comparison of the nature of the polymer and the scale control activity as described by the prior art given supra, suggests that lowering the molar ratio of the maleic anhydride moiety to other monomer moieties in copolymers of terpolymers so composed will decrease both the charge density and the scale control activity. For example, the scale control data recorded for the polymers of GB 1414918 reveal that the activity against calcium carbonate precipitation decreases when progressing through the set of activities associated with homomaleic anhydride polymer through maleic anhydride-acrylamide copolymer to maleic anhydride-vinyl acetate-ethyl acrylate terpolymer. The same trend is apparent from a correlation of the scale control activities of the polymers of Dutch application 7506874.

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When the ratio of maleic anhydride portion to other monomer portion in the test polymer formed according to that application is decreased, the activity against calcium carbonate precipitation decreases. Thus, the literature teaches that the use of non-carboxylic acid monomers in conjunction with maleic anhydride monomer to form a polymer of mixed composition will cause a decrease in the scale control activity of that polymer relative to hydrolyzed polymaleic anhydride.

As is true for most polymers, the method used in preparing the scale control polymer will influence its nature and activity independent of the relative ratios of monomers used. General methods for the preparation of scale control polymers are described in U.S. 3,755,264, and U.S. 3,359,246, in addition to the methods contained in the patents describing use, supra. Although this prior art gives a wealth of information on how to prepare maleic anhydride and/or acrylic acid polymers, in practice, these preparation methods often lead to uncontrollable polymerization rates, the Trommsdorff effect, gelling and gumming of the polymers during polymerization, failure to control the magnitude and range of polymer molecular weight, impractical long polymerization times, and the unsafe nature of the reaction.

In view of the methods of preparation and suggestions of activity of the prior art it is surprising to discover that an interplay of monomer composition, temperature and reaction solvent according to the present invention allows the preparation of novel granular maleic anhydride terpolymer which has a controlled molecular weight range and is low in maleic anhydride content but nevertheless has scale control activity approximating that of hydrolyzed polymaleic anhydride. The novel process can also be employed to prepare useful maleic anhydride copolymers which are granular and readily processed.

According to the present invention there is provided a terpolymer, its hydrolysed form, and the alkali metal, amine and ammonium salts of said hydrolysed form, consisting of (a) 30-55 mole percent of maleic anhydride (b) 30-65 mole percent of acrylamide or methacrylamide, and (c) 5-15 mole percent of a third monomer selected from styrene, α -methyl styrene, alkyl acrylates and alkyl methacrylates having 1 to 8 carbon atoms in the alkyl group, and 1-alkenes having 4 to 10 carbon atoms, said terpolymer being characterized by a relative viscosity of 1.02 to 1.10 in dimethylsulfoxide at a concentration of 0.5 grams per deciliter; by a solubility of less than 0.10 g. per g. of solution (water) at ambient temperature and preferably by substantial freedom from unreacted monomer.

Also according to the invention there is provided a copolymer consisting of (a) 28.2 to 70 (preferably 30 to 70) mole percent of maleic anhydride and (b) 30 to 71.8 (preferably 30 to 70) mole percent of acrylamide or methacrylamide, said copolymer being characterized by a relative viscosity and solubility as defined above.

The terpolymers of the present invention have a preferred solubility of less than 0.06 g. per g. of solution (water).

A terpolymer composition wherein the third monomer is styrene is preferred because of the favorable balance of scale control activity and hydrophobicity of its hydrolyzed form. A preferred monomer ratio of this terpolymer is 30 to 50 mole percent maleic anhydride, 40 to 55 mole percent acrylamide and 5 to 15 mole percent styrene. Particularly preferred is a monomer ratio of 41 to 45 mole percent maleic anhydride, 45 to 49 mole percent acrylamide and 9 to 13 mole percent styrene. A preferred copolymer composition is a copolymer consisting of 45 to 55 mole percent maleic anhydride and 45 to 55 mole percent acrylamide.

In addition the present invention comprises a method for the prevention of scale formation when heating or desalinating water containing scale forming impurities such as water being sea water, boiler water, water with calcium and magnesium cations and other similarly impure forms of water, which comprises mixing with said water the hydrolyzed form of a terpolymer, or an alkali metal, amine or ammonium salt thereof, which terpolymer consists of (a) 30 to 55 mole percent of maleic anhydride, (b) 30 to 65 mole percent of acrylamide or methacrylamide, and (c) 5 to 15 mole percent of a third monomer as described supra to make a concentration of the hydrolyzed or salt form of the terpolymer in water of at least 2 parts per million and wherein the unhydrolyzed terpolymer is as characterized supra. A preferred method of treatment employs a terpolymer wherein the third monomer is styrene. A more preferred method of treatment employs a terpolymer consisting essentially of 41 to 46 mole percent maleic anhydride, 45 to 49 mole percent acrylamide and 9 to 13 mole percent styrene.

A further feature of the present invention is the process used to prepare the above described terpolymers and copolymers. It allows isolation of the polymer as a granular precipitate rather than as a gum, a resin or an oil, and is one which causes the resultant polymer to be insoluble in water at ambient temperature. It is believed this insolubility is the result of a rearrangement of the chemical structure of the polymer; but not withstanding that view the insolubility is definitely related to the heat and solvent interplay of the reaction process. Most likely the process acts to form a substantial number of imide

moieties along the polymer backbone by causing the recombination of the anhydride moiety of the maleic anhydride fragments with the amide moiety of the acrylamide fragments. The theorized imide moieties in turn then cause the observed insolubility. Additional insolubility in the terpolymer series is caused by the hydrophobicity of the third monomer.

To obtain the desired insolubility in water at ambient temperature and granular precipitate formation, it is necessary to employ reaction temperatures of at least 120°C and a chain transfer solvent or mixture thereof which has a propensity for free radical abstraction, has a polarity greater than that of toluene, will enter into the polymerization chain reaction, and will not allow swelling or agglomeration of the formed particulate polymer.

The water insolubility of the polymer can be used to advantage in the purification. Slurrying the crude reaction polymer in cold water will dissolve the water soluble monomers leaving the polymer substantially free of unreacted monomer. In this manner, potential contamination of the desalination process by residual monomer is avoided.

Thus according to a further aspect of the invention there is provided a process for the preparation of a terpolymer as previously defined which process comprises heating a mixture of said maleic anhydride and said acrylamide or methacrylamide in the appropriate proportions in a chain transfer solvent mixture to at least 120°C, introducing said third monomer and from 2 to 20 weight percent based on the total weight of the monomers of a free radical initiator and continuing to maintain said mixture at a temperature of at least about 120°C until polymerization is essentially complete, said chain transfer solvent mixture being: (i) from 15 to 85 weight percent of an aromatic solvent selected from mono and dialkyl substituted benzenes having from 1 to 4 carbon atoms in each alkyl group and trialkyl substituted benzenes having from 1 to 2 carbon atoms in each alkyl group, and (ii) from 15 to 85 weight percent of a ketone solvent selected from dialkyl ketones having from 1 to 5 carbon atoms in each alkyl group, the alkyl groups being the same or different, and cycloalkanones having from 5 to 8 carbon atoms in the cycloalkyl group.

The novel insolubility in water at ambient temperature which is present in the terpolymers of the present invention can be generated in maleic anhydride-acrylamide copolymers of the present invention as well by employing the process of the present invention. Observation of this effect in the copolymers lends support to the idea that the insolubility in either type of polymer of the present invention is caused mainly by the presence of the imide moiety and that the obvious hydrophobic effect of the third monomer in the terpolymer is supplementary.

The reaction parameters necessary to obtain the desired transformation during polymerization are high and similar molar quantities of the anhydride and acrylamide monomers, temperature, solvent and for the terpolymer, mode of addition of the third monomer. These are critical for the successful outcome and provide the necessary conditions to obtain the novel insolubility.

The temperature requirement for the reaction process is at least 120°C, and this may be achieved by applying pressure when employing solvents which boil at lower temperatures at atmospheric pressure. The upper limit of the range will depend on the controllability of the reaction rate and on the reflux temperature of the solvent or mixture thereof provided that the employed solvent or mixture thereof boils at a temperature higher than 120°C. The preferred temperature employed is that of refluxing solvent and is usually within the range of 125° to 150°C.

The time parameter of the reaction will vary according to the particular starting materials used. The usual course of the polymerization can be followed by observing the precipitation of the polymer as fine particulate granules, and the polymerization is substantially complete when precipitation ceases. The total time period is usually within the range of 1 to 10 hours and the most frequent time period observed is approximately 2 hours.

The reaction solvents used in the process of the present invention are reactive; in other words, they enter into the chain propagation and termination steps of the polymerization. They include alkyl substituted benzenes such as toluene, xylene, mesitylene, ethyl benzene and propyl benzene, and aliphatic ketones and cycloalkyl ketones such as methyl ethyl ketone, acetone, 4-methyl-2-pentanone, cyclohexanone, dibutylketone, dipropylketone, and other similar aromatic and ketonic organic liquid solvents. The process employs a mixture of the aromatic solvent and the ketone solvent at ratios of 15 to 85 weight percent ketone solvent to 15 to 85 weight percent aromatic solvent. The relative proportions selected in a given case will depend upon the nature of the particular polymer being formed. But, in general, these ratios will insure that the polymer will not agglomerate or swell during its formation.

A preferred chain transfer solvent mixture is a mixture of substantially equal amounts of xylene and methyl isobutyl ketone.

Any free radical initiator capable of initiating a free radical reaction may be used in the process. Typical initiators include di-*t*-butyl peroxide, benzoyl peroxide, azobisisobutyronitrile, dicumyl peroxide and dilauroyl peroxide. Although the weight ratio of initiator to monomer will vary according to the particular monomers used, the range is usually from 2 to 20 weight percent based upon total monomers.

In accordance with these reaction parameters, a terpolymer of the present invention is formed by first contacting from 30 to 55 mole percent maleic anhydride with from 30 to 65 mole percent acrylamide or methacrylamide in the appropriate reaction solvent. The mixture is heated to the appropriate temperature, and the free radical initiator, and from 5 to 15 mole percent third monomer, described supra, each dissolved in the reaction solvent, are then added to the reaction mixture, preferably at such a rate so as to complete addition within a time period of from 15 to 180 minutes. The usual rate-of-addition time period is approximately 30 to 60 minutes.

To form a copolymer of the present invention, from 28.2 to 70 mole percent maleic anhydride is contacted with from 30 to 71.8 mole percent acrylamide or methacrylamide in the same manner as that described for the terpolymers except that the third monomer is omitted.

The reaction is preferably conducted under an inert atmosphere, e.g., nitrogen.

Agitation of the reaction mixture is preferably maintained throughout the course of the reaction, e.g., by stirring or sparging.

Isolation of the polymer can be accomplished by any of the standard techniques available and known to the art. The usual method is concentration of the reaction medium by evaporation, filtration and subsequent slurring of the filtered solids with cold water (below 30°C) to dissolve unreacted monomer. This will yield polymer substantially free of unreacted monomer. Other methods include washing the filtered reaction material with organic solvents such as ether, tetrahydrofuran, chloroform, carbon tetrachloride and similar nonpolar, nonhydroxylic organic solvents.

The polymer is then prepared for scale control use by hydrolysis in refluxing water. The process for conversion of the insoluble polymer to soluble, hydrolyzed polymer usually requires six to ten hours. Alternatively, the polymer can be hydrolyzed by stirring it with 0.1 to 4 molar aqueous sodium hydroxide at temperatures in the range of 25-100°C.

The alkali metal, and ammonium salts of the hydrolyzed terpolymer can be formed by adding the alkali metal base, ammonia or organic amine to the water solution of the hydrolyzed terpolymer or by employing the base directly to hydrolyze the unhydrolyzed terpolymer. Subsequent evaporation of the water will allow isolation of the desired terpolymer salt or it may be used directly in aqueous solution without isolation. Common alkali metal bases include sodium hydroxide, potassium hydroxide and lithium hydroxide. Common ammonium bases and amines include ammonium hydroxide, ammonia, mono-, di-, and trialkyl amines having from 1 to 5 carbon atoms in each alkyl group, pyridine, morpholine and lutidine.

The hydrolyzed terpolymers of the invention and the corresponding salts of the invention may be used for the prevention of scale formation when heating or desalinating water containing scale forming impurities such as those present in sea water, boiler water, water with calcium and magnesium ions and other similarly impure forms of water. The solid hydrolyzed terpolymer or salts thereof may be directly introduced into the water containing scale forming impurities so as to make a concentration in the water of at least 2 parts per million. Alternatively, the hydrolyzed terpolymer or salts thereof may be introduced into the water containing scale forming impurities by use of a concentrated aqueous solution to form a concentration in the water of at least 2 parts per million. This treatment may be performed as understood by those familiar with the art in any manner consistent with processes used to treat water. Thus, if a batch desalination operation is being used, the scale control agent of the invention will be introduced in batch amounts. On the other hand, if a continuous desalination operation is being used, the scale control agent may be continuously added into the recirculating pipeline for the water containing scale forming impurities or may be added to the source which serves as the holding tank for the continuous desalination. Scale control in boiler applications is achieved in the same manner. As is readily apparent to those skilled in the art, the operation will require shut down from time to time to remove the concentrated impurities suspended by agent in the pot or boiler. However, the cleanout operation will usually be a simple drainage and flushing of the pot or boiler rather than the difficult cleanout needed to remove scale deposit.

The characteristic insolubility in water at ambient temperature of the terpolymers and copolymers of the present invention is displayed in Table I. It was determined by stirring a mixture of 25 weight percent polymer in distilled water at room temperature for 3 hours followed by removal of the liquid phase. The dissolved polymer was then recovered from

the liquid phase by freeze drying the solution and both this material and the insoluble polymer were oven dried at 25° over phosphorus pentoxide in a 0.1 torr vacuum for approximately two days. The weights of the dissolved and insoluble polymer were compared for mass balance and recorded as the solubility behavior in grams of polymer dissolved per gram of solution for that particular composition. The polymer of method A which was chosen for comparison was prepared according to the general method provided by U.K. 1,414,918.

To demonstrate that insolubility was not time related, the terpolymer listed on Table I was stirred for two days in the same manner and proportions as described supra. After two days of stirring at ambient temperature, the polymer was isolated in the same manner as before and has a solubility of 0.0408 g. per g. of solution.

A comparison (Table I) of the solubility behavior of the polymers of the present invention with that of the polymer of Method A shows the dramatically different solubility characteristics of the polymers of the present invention. The explanation for the lack of water insolubility of the polymer of method A is apparent from a comparison of the process to make it with the process of the present invention (compare Method A with Example 8). The polymerization temperature is higher in the method of this invention (at least 120° as compared to the range of 70° to 110° for Method A) and a mixture of aromatic and ketone solvent is employed. The result is that the necessary conditions are provided by the process of the present invention to cause the novel insolubility in water at ambient temperature which is believed to be allied with the production of amide moieties in the co- and terpolymers.

TABLE 1

Polymer insolubility

Polymer composition (mole percent based on analysis)		Example no.	Solubility behavior (g. of polymer dissolved per g. of solution)
49 maleic anhydride 51 acrylamide		8	0.058
29 maleic anhydride 71 acrylamide		10	0.080
46 maleic anhydride 54 methacrylamide		9	0.073
43 maleic anhydride 46 acrylamide 11 styrene		1	0.050
58.4 maleic anhydride 41.7 acrylamide		method (A)	polymer completely dissolved

(The solubilities of the polymer of Examples 2 to 7 were less than 0.050 g. per g. of solution)

The scale inhibitor activity of the hydrolyzed terpolymers of the present invention was determined by measuring the amount of precipitate formed upon heating under pressure a standard solution of synthetic sea water containing the added terpolymer scale inhibitor. The procedure and results are given in Example 11 and they are to be compared to two types of controls, one employing no agent, and the other employing polymaleic acid (formed according to the methods given in U.K. 1,414,918). These results demonstrate that although the charge density of the present hydrolyzed terpolymers has been reduced relative to that of polymaleic acid and their hydrophobicity has been increased, the hydrolyzed terpolymers of the present invention have significant scale inhibitor activity which is approximately equal to that of polymaleic acid. It is postulated that the hydrolyzed terpolymers of the present invention operate through a threshold mechanism of scale control where binding of the hydrolyzed terpolymer to the crystal nuclei growing site inhibits further crystal growth at that site and the hydrophobicity of the third monomer contained in the bound terpolymer repels the incoming polar water cage containing the solubilized inorganic ions.

The following examples 1 to 11 are merely illustrative of the invention and are in no way to be construed as limiting the scope of the claims. (Example A is a comparative example).

All temperatures are in degrees Centigrade and if not specified are ambient temperature. The infrared spectra were obtained on a Perkin-Elmer IR-21 grating spectrophotometer and are listed in microns.

The viscosity measurements which were used to calculate the molecular weight of the polymers were conducted in the standard manner with a Ubbelohde Viscometer by employing a solution of 0.5 gram of the polymer in 100 milliliters of dimethylsulfoxide at $25 \pm 0.01^\circ\text{C}$. The viscosity measured was the relative viscosity (N) which is defined as $n = t/t_0$ where t equals the flow time in seconds of the polymer solution and t_0 equals the flow time in seconds of the solvent.

METHOD A

Copolymer (A) of maleic anhydride and acrylamide formed according to the method of U. K. 1,414,918.

A solution of 46.5 g (0.474 moles, 71.4 mole %) of maleic anhydride, 13.5 g (0.190 moles, 28.6 mole %) of acrylamide and 143.0 g of toluene was stirred and heated under a nitrogen atmosphere until a temperature of 70° was reached. To the solution was then added a solution of 12.0 g 20 wt. % benzoyl peroxide in 70.0 g toluene over a period of five minutes. The solution was then refluxed at 110°C . to 113° for 6 hours. After cooling, the toluene solution was decanted from the resinous material which was purified by triturating with benzene. There was obtained a 63% yield of copolymer A having a relative viscosity of 1.04.

Copolymer A composition as determined by CHN analysis:

58.4 mole % maleic anhydride

41.7 mole % acrylamide.

EXAMPLE 1

Terpolymer (1) of maleic anhydride, acrylamide and styrene

Into a four neck 2000 ml round bottom flask equipped with a reflux condenser and mechanical stirrer was added 150.0 gms (1.53 moles, 45 mole %) maleic anhydride, 108.8 gms. (1.53 moles, 45 mole %) acrylamide, 235.0 gms methyl isobutyl ketone and 235.0 gms xylene. The system was sparged with nitrogen and then the flask was lowered into an oil bath maintained at 150°C and as the reaction mixture warmed, formed a solution. When gentle refluxing was achieved at a reaction mixture temperature of 126° to 130° , the solution of free radical initiator consisting of 14.71 gm di-*t*-butyl peroxide, 16.0 gm methyl isobutyl ketone and 16.0 gm xylene was added continuously at such a rate so as to complete addition in 30 minutes. Simultaneously a solution of third monomer consisting of 35.4 gm (0.340 mole, 10 mole%) styrene, 29.0 gm methyl isobutyl ketone and 29.0 gm xylene was added continuously at such a rate so as to complete addition in 60 minutes. During and following third monomer addition, the polymer precipitated as a fluid reaction slurry. After polymerization was substantially complete, 2 hours, the polymerization mixture was allowed to cool to room temperature, filtered, and the precipitate washed with diethyl ether and vacuum oven dried at 80°C for 17 hours. Alternatively, the precipitate may be washed with water and vacuum oven dried. The resulting tan colored free flowing powder terpolymer 1 was obtained in 87.6% yield and had a relative viscosity of 1.04.

Terpolymer 1 composition as determined from CHN analysis:

43 mole % maleic anhydride

46 mole % acrylamide

11 mole % styrene

IR (KBr) 2.94, 3.02, 5.42, 5.64, 5.80, 5.86, 6.05, 6.22, and 8.40μ .

The other terpolymers of the present invention can be prepared according to the procedure of Example 1 by substituting the appropriate monomers at the appropriate ratio for those of Example 1.

EXAMPLE 2

Terpolymer (2) of maleic anhydride, acrylamide and styrene

The terpolymer 2 was prepared according to the procedure of Example 1 by employing the same mole percent ratios of monomers but by substituting the solvent ratio 75 wt. % methyl isobutyl ketone, 25 wt. % xylene for that of Example 1. There was obtained an 87.5% yield of free-flowing powdery terpolymer 2 having a relative viscosity of 1.04.

Terpolymer 2 composition as determined by CHN analysis:

43 mole % maleic anhydride

47 mole % acrylamide

10 mole % styrene.

IR spectrum (KBr) identical to that of terpolymer 1.

EXAMPLE 3*Terpolymer (3) of maleic anhydride, acrylamide and styrene*

The terpolymer 3 was prepared according to the procedure of Example 1 by substituting the monomer ratios 55 mole % maleic anhydride, 35 mole % acrylamide and 10 mole percent styrene for those of Example 1. There was obtained an 88.1% yield of free flowing granular terpolymer 3 having a relative viscosity of 1.04.

Terpolymer 3 composition as determined by CHN analysis:

50.98 mole % maleic anhydride

35.5 mole % acrylamide

13.4 mole % styrene.

IR spectrum (KBr) identical to that of terpolymer 1.

EXAMPLE 4*Terpolymer (4) of maleic anhydride, acrylamide and styrene*

Terpolymer 4 was prepared according to the procedure of Example 1 by employing the same monomer ratio but by substituting dicumyl peroxide for di-*t*-butyl peroxide on an equimolar basis. There was obtained an 88.2% yield of granular terpolymer 4 having a relative viscosity of 1.03_g.

Terpolymer 4 composition as determined by CHN analysis:

44.5 mole % maleic anhydride

44.6 mole % acrylamide

10.9 mole % styrene.

IR spectrum (KBr) identical to that of terpolymer 1.

EXAMPLE 5*Terpolymer (5) of maleic anhydride, acrylamide and 1-octene*

Into a flask was added 183.4 gm (1.871 moles, 55 mole %) maleic anhydride, 72.5 gm (1.021 moles, 30 mole %) acrylamide, 215.0 gm methyl isobutyl ketone and 215.0 gm xylene. The system was sparged for 1.5 hrs. with nitrogen, and then it was lowered into an oil bath maintained at 150°C. When gentle refluxing was achieved at a reaction mixture temperature of 126° to 130°, a solution consisting of 31.3 gm dicumyl peroxide, 36.0 gm methyl isobutyl ketone and 36.0 gm xylene was added dropwise over a period of 1 hr. Simultaneously a solution consisting of 57.3 gm (0.510 mole, 15 mole %) 1-octene, 47.0 gm methyl isobutyl ketone and 47.0 gm xylene was added dropwise over a period of 0.5 hr. After polymerization was substantially complete, 4.0 hrs, the reaction mixture was allowed to cool. The particulate terpolymer was filtered, washed with excess diethyl ether, and vacuum oven dried at approximately 90°C. There was obtained a 56% yield of tan-colored, free-flowing, powder, terpolymer 5 having a relative viscosity of 1.04_g.

Terpolymer 5 composition as determined from CHN analysis:

50.9 mole % maleic anhydride

41.2 mole % acrylamide

7.85 mole % 1-octene

IR spectrum (KBr) was similar to that of terpolymer 1.

EXAMPLE 6*Terpolymer (6) of maleic anhydride, methacrylamide and styrene*

Terpolymer 6 was prepared according to the procedure of Example 1 by substituting methacrylamide for acrylamide at the same mole % ratio. There was obtained a 95% yield of granular terpolymer 6 having a relative viscosity of 1.05_g.

Terpolymer 6 composition as determined by CHN analysis:

42.8 mole % maleic anhydride

46.7 mole % methacrylamide

10.3 mole % styrene

EXAMPLE 7*Terpolymer (7) of maleic anhydride, acrylamide and alpha-methyl styrene*

Terpolymer 7 was prepared according to the procedure of Example 1 by substituting alpha methyl styrene for styrene at the same mole % ratio. There was obtained an 89.4% yield of granular terpolymer 7 having a relative viscosity of 1.04_g.

Terpolymer 7 composition as determined by CHN analysis:

44.5 mole % maleic anhydride

44.9 mole % acrylamide

10.9 mole % alpha methyl styrene

EXAMPLE 8*Copolymer (8) of maleic anhydride and acrylamide*

To a four neck 2000 ml round bottom flask equipped with a mechanical stirrer, N₂ inlet, cold water condenser and thermometer was added 150.0 gms (1.53 moles, 50 mole %) maleic anhydride, 108.7 gms (1.53 moles, 50 mole %) acrylamide, 224.0 gms 4-methyl-2-pentanone and 224.0 gms xylene. The mixture was stirred at room temperature and sparged with nitrogen for 15 min. Then, the system was lowered into an oil bath maintained at 130°C and at 60°C the solid starting materials dissolved. When the solution was refluxing gently, at a temperature of 126° to 130°, a solution of 12.98 gms (10 wt %) di-t-butyl peroxide, 16.0 gms methyl isobutyl ketone and 16 gms xylene was added dropwise over a period of 30 min. Upon addition of the initiator, polymer precipitation occurred. After 1 hour a second solution consisting of 12.98 gms di-t-butyl peroxide and 112.5 gms xylene was added dropwise to the polymerizing medium over a 2 hour period. The polymerization was allowed to continue for an additional hour after which the dispersion-like mixture was cooled to room temperature, the precipitate filtered, washed with diethyl ether and vacuum oven dried at 90°C. Alternatively, the precipitate may be washed with water and vacuum oven dried. There was obtained an 89.6% yield of free flowing powder copolymer 8 having a relative viscosity of 1.05.

Copolymer composition as determined from CHN analysis:

49 mole % maleic anhydride

51 mole % acrylamide.

IR spectrum (KBr) 2.94, 3.02, 5.43, 5.65, 5.86, 6.02, 6.20 and 8.45μ.

The other copolymers of the present invention can be synthesized according to the procedure of Example 8 by substituting the appropriate monomers at the appropriate ratio for those of Example 8.

EXAMPLE 9*Copolymer (9) of maleic anhydride and methacrylamide*

Copolymer 9 was prepared according to the procedure of Example 6 by omitting the styrene monomer. There was obtained an 85% yield of free flowing, powdery copolymer 9 having a relative viscosity of 1.05.

Copolymer composition as determined by CHN analysis:

46 mole % maleic anhydride

54 mole % methacrylamide.

IR spectrum 2.96, 3.03, 5.45, 5.65, 5.80, 5.86, 6.02, 6.25 and 8.23μ.

EXAMPLE 10*Copolymer (10) of maleic anhydride and acrylamide*

Copolymer 10 was prepared according to the procedure of Example 8 by substituting 25 mole % maleic anhydride and 75 mole % acrylamide for those monomer ratios of Example 8. There was obtained a 96.7% yield of free flowing, powdery copolymer 10 having a relative viscosity of 1.10.

Copolymer composition from CHN analysis:

71.8 mole % acrylamide

28.2 mole % maleic anhydride.

EXAMPLE 11*Scale inhibitor activity of the hydrolyzed polymers of Examples 1 through 10*

Synthetic sea water was made by dissolving the following weights of inorganic salts in one liter of distilled water: NaCl, 26.5 gm; MgCl₂, 2.4 gm; MgSO₄, 3.3 gm; CaCl₂, 1.1 gm; KCl, 0.72 gm; NaHCO₃, 0.245 gm; and NaBr, 0.08 gm.

To conduct the test, a 1.0 ml aliquot of a 0.1% aqueous solution of the hydrolyzed polymer was added to a beaker containing 166 ml. of synthetic sea water and Monel (Registered Trade Mark) foil, 1 inch square. The test beaker and a positive control beaker containing 166 ml sea water, 1.0 ml of a 0.1% aqueous solution of polymaleic acid (prepared according to the method of U.K. 1,414,918) and a 1 inch square Monel foil were placed in an autoclave (pressure cooker) containing a stirrable 10% aqueous lithium chloride solution. The pressure relief valve of the autoclave was set at 10 psi so that the boiling point of the sea water sample would be elevated to 115°C. and the autoclave was closed and heated until steam started to escape through the relief valve (20 to 30 min). Heating was continued for 45 min after which the autoclave was allowed to cool. When the internal pressure of the autoclave decreased to atmospheric pressure, control and sample beakers were removed and cooled in a 25°C. water bath. Each beaker was analyzed separately as follows. The Monel foil was removed and rinsed with 50 ml of 6N HCl to remove any scale formed. The final volume of sea water was measured and the amount

evaporated calculated. The sea water was filtered through a 0.2 micron cellulosic membrane filter to collect the precipitate formed and the acid used to wash the Monel foil was passed slowly through the filter to dissolve the precipitate. The volume of the acid solution was then measured and the amount of calcium and/or magnesium compounds precipitated was measured by EDTA titration of an aliquot of the acid wash. A total of four test samples and four positive control samples were run and the averages and standard deviations computed. The amount of water lost was also averaged and the standard deviation found. It was calculated as the percent of the total amount and expressed as percent evaporation. The positive control average and their percent evaporations were compared to a table of scale depositions versus percent evaporations for polymaleic acid which was of the same type and source as for Table III contained herein. The comparison was used to assure that nothing abnormal had occurred during the test.

The averaged results of the scale control test using each of the various Example polymers of the present invention are recorded on Table II as millequivalents of EDTA complexed calcium/magnesium along with the results from a test on a null control (test using no scale control) polymer. The percent evaporation is recorded on Table II in conjunction with the average scale result.

In order to compare the scale control activity of the test polymers to that of the positive control, a polymaleic acid, it was necessary first to ascertain what effect the amount of evaporation had on the scale deposition. Assuming that the positive standard for comparison was polymaleic acid, and that the percent evaporation was mainly a function of the apparatus and the test conditions and not the identity of the scale control agent, such a determination was made by repeatedly testing polymaleic acid as a scale control agent under the above described experimental conditions. The amounts of scale deposition from each test which fell within each 0.6 percent evaporation increment starting at 12% evaporation were averaged and the mean deviation of each average was calculated. These averages and their respective evaporation ranges are presented on Table III.

Using the data from Table III, the performance of the Example polymers as scale control agents can be compared with the performance of polymaleic acid. After selecting the range increment for percent evaporation from Table III in which the percent evaporation for the Example polymer in question would fall, the average scale for that range increment from Table III is compared to the Sample average scale for the Example polymer in question from Table II. If the Example polymer "Sample Average Scale" value is lower than the corresponding Average Scale value for polymaleic acid, then the Example polymer is a more active scale control agent than polymaleic acid. When considering this comparison, the spread of both the Sample average scale values and the polymaleic acid scale values should be taken into account in order to judge the merits of the Example polymers as scale control agents relative to the merits of the positive standard, polymaleic acid.

TABLE II

Scale control activity of the hydrolyzed example polymers

Polymer example no. (hydrolyzed polymer)	Sample avg. scale (meq)	std. dev.	Avg. (%)	Ev. std. dev.
1	0.102	0.028	15.1	1.5
2*	0.158	0.039	13.6	1.8
3	0.080	0.008	13.0	0.6
4	0.079	0.028	13.6	0.6
5*	0.143	0.023	15.4	1.4
6	0.149	0.046	14.9	1.6
7	0.073	0.026	12.3	0.7
8*	0.149	0.015	15.3	1.2
9	0.110	0.060	15.9	1.2
10	0.115	0.032	15.5	2.4
- Null control	0.200	0.005	15.0	2.4

* Both the amount of sample scale and the amount of positive control scale (polymaleic acid) deposited during the test runs for these Examples were abnormally high, e.g. for 2 the avg. scale deposited for polymaleic acid during that particular test was 0.127; for 5 it was 0.148 and for 8 it was 0.15.

TABLE III

Scale deposition as a function of percent evaporation using polymaleic acid as a scale control agent

	Percent evaporation range	Average scale found (meq.)	Mean deviation	
5	12.0-12.6	0.065	±0.013	5
10	12.6-13.2	0.075	±0.003	10
	13.2-13.8	0.081	±0.007	
	13.8-14.4	0.106	±0.010	
	14.4-15.0	0.117	±0.009	
15	15.0-15.7	0.119	±0.004	15

WHAT WE CLAIM IS:-

1. A terpolymer consisting of (a) 30 to 55 mole percent of maleic anhydride, (b) 30 to 65 mole percent of acrylamide or methacrylamide, and (c) 5 to 15 mole percent of a third monomer selected from styrene, α -methyl styrene, alkyl acrylates and alkyl methacrylates having from one to eight carbon atoms in the alkyl group, and 1-alkenes having from four to ten carbon atoms, said terpolymer being characterized by a relative viscosity of 1.02 to 1.10 in dimethyl sulfoxide at a concentration of 0.5 g per deciliter, and by a solubility of less than 0.10 g per g. of solution (water) at ambient temperature; or the hydrolyzed form thereof;
- 25 or an alkali metal, amine or ammonium salt of said hydrolyzed form.
2. A terpolymer as claimed in claim 1 wherein said third monomer is styrene.
3. A terpolymer as claimed in claim 2 consisting of 30 to 50 mole percent maleic anhydride, 40 to 55 mole percent acrylamide and 5 to 15 mole percent styrene.
- 30 4. A terpolymer as claimed in claim 3 consisting of 41 to 45 mole percent maleic anhydride, 45 to 49 mole percent of acrylamide and 9 to 13 mole percent styrene.
5. The hydrolyzed form of the terpolymer of claim 1.
6. The hydrolyzed form of the terpolymer of claim 4.
7. An alkali metal or ammonium salt of the hydrolyzed terpolymer of claim 5.
8. An alkali metal or ammonium salt of the hydrolyzed terpolymer of claim 6.
- 35 9. A process for preparing a terpolymer as claimed in claim 1 which comprises: heating a mixture of said maleic anhydride and said acrylamide or methacrylamide in the appropriate proportions in a chain transfer solvent mixture to at least 120°C, introducing in the appropriate proportions said third monomer and from 2 to 20 weight percent based on the total weight of the monomers of a free radical initiator and continuing to maintain said mixture at a temperature of at least 120°C until polymerization is essentially complete, said chain transfer solvent mixture being (i) from 15 to 85 weight percent of an aromatic solvent selected from mono and dialkyl substituted benzenes having from 1 to 4 carbon atoms in each alkyl group and trialkyl substituted benzenes having 1 or 2 carbon atoms in each alkyl group, and (ii) from 15 to 85 weight percent of a ketone solvent selected from dialkyl ketones having from 1 to 5 carbon atoms in each alkyl group, the alkyl groups being the same or different, and cycloalkanones having from 5 to 8 carbon atoms in the cycloalkyl group.
10. A process as claimed in 9 which includes the steps of isolating said terpolymer after polymerization and treating said terpolymer with water at a temperature below 30°C to remove any unreacted monomer.
- 50 11. A process as claimed in claim 9 or 10 wherein the terpolymer prepared consists of 41 to 45 mole percent maleic anhydride, 45 to 49 mole percent acrylamide and 9 to 13 mole percent styrene.
12. A process as claimed in any one of the preceding claims 9 to 11 wherein in said chain transfer solvent mixture component (i) is xylene and component (ii) is methyl isobutyl ketone.
- 55 13. A process as claimed in any one of claims 9 to 12 wherein said mixture is maintained at 125 - 150°C until polymerisation is substantially complete, and wherein said free radical initiator is di-*t*-butyl peroxide or dicumyl peroxide.
- 60 14. A copolymer consisting of (a) 28.2 to 70 mole percent of maleic anhydride and (b) 30 to 71.8 mole percent of acrylamide or methacrylamide, said copolymer being characterized by a relative viscosity of 1.02 to 1.10 in dimethyl sulfoxide at a concentration of 0.5 g per deciliter and by solubility of less than 0.10 g per g. of solution (water) at ambient temperature.
- 65 15. A copolymer as claimed in claim 14 consisting of 30 to 70 mole percent of maleic



TABLE III

Scale deposition as a function of percent evaporation using polymaleic acid as a scale control agent

5	Percent evaporation range	Average scale found (meq.)	Mean deviation	5
	12.0-12.6	0.065	±0.013	
10	12.6-13.2	0.075	±0.003	10
	13.2-13.8	0.081	±0.007	
	13.8-14.4	0.106	±0.010	
	14.4-15.0	0.117	±0.009	
15	15.0-15.7	0.119	±0.004	15

WHAT WE CLAIM IS:-

1. A terpolymer consisting of (a) 30 to 55 mole percent of maleic anhydride, (b) 30 to 65 mole percent of acrylamide or methacrylamide, and (c) 5 to 15 mole percent of a third monomer selected from styrene, α -methyl styrene, alkyl acrylates and alkyl methacrylates having from one to eight carbon atoms in the alkyl group, and 1-alkenes having from four to ten carbon atoms, said terpolymer being characterized by a relative viscosity of 1.02 to 1.10 in dimethyl sulfoxide at a concentration of 0.5 g per deciliter, and by a solubility of less than 0.10 g per g. of solution (water) at ambient temperature; or the hydrolyzed form thereof;
2. A terpolymer as claimed in claim 1 wherein said third monomer is styrene.
3. A terpolymer as claimed in claim 2 consisting of 30 to 50 mole percent maleic anhydride, 40 to 55 mole percent acrylamide and 5 to 15 mole percent styrene.
4. A terpolymer as claimed in claim 3 consisting of 41 to 45 mole percent maleic anhydride, 45 to 49 mole percent of acrylamide and 9 to 13 mole percent styrene.
5. The hydrolyzed form of the terpolymer of claim 1.
6. The hydrolyzed form of the terpolymer of claim 4.
7. An alkali metal or ammonium salt of the hydrolyzed terpolymer of claim 5.
8. An alkali metal or ammonium salt of the hydrolyzed terpolymer of claim 6.
9. A process for preparing a terpolymer as claimed in claim 1 which comprises: heating a mixture of said maleic anhydride and said acrylamide or methacrylamide in the appropriate proportions in a chain transfer solvent mixture to at least 120°C, introducing in the appropriate proportions said third monomer and from 2 to 20 weight percent based on the total weight of the monomers of a free radical initiator and continuing to maintain said mixture at a temperature of at least 120°C until polymerization is essentially complete, said chain transfer solvent mixture being (i) from 15 to 85 weight percent of an aromatic solvent selected from mono and dialkyl substituted benzenes having from 1 to 4 carbon atoms in each alkyl group and trialkyl substituted benzenes having 1 or 2 carbon atoms in each alkyl group, and (ii) from 15 to 85 weight percent of a ketone solvent selected from dialkyl ketones having from 1 to 5 carbon atoms in each alkyl group, the alkyl groups being the same or different, and cycloalkanones having from 5 to 8 carbon atoms in the cycloalkyl group.
10. A process as claimed in 9 which includes the steps of isolating said terpolymer after polymerization and treating said terpolymer with water at a temperature below 30°C to remove any unreacted monomer.
11. A process as claimed in claim 9 or 10 wherein the terpolymer prepared consists of 41 to 45 mole percent maleic anhydride, 45 to 49 mole percent acrylamide and 9 to 13 mole percent styrene.
12. A process as claimed in any one of the preceding claims 9 to 11 wherein in said chain transfer solvent mixture component (i) is xylene and component (ii) is methyl isobutyl ketone.
13. A process as claimed in any one of claims 9 to 12 wherein said mixture is maintained at 125 - 150°C until polymerisation is substantially complete, and wherein said free radical initiator is di-*t*-butyl peroxide or dicumyl peroxide.
14. A copolymer consisting of (a) 28.2 to 70 mole percent of maleic anhydride and (b) 30 to 71.8 mole percent of acrylamide or methacrylamide, said copolymer being characterized by a relative viscosity of 1.02 to 1.10 in dimethyl sulfoxide at a concentration of 0.5 g per deciliter and by solubility of less than 0.10 g per g. of solution (water) at ambient temperature.
15. A copolymer as claimed in claim 14 consisting of 30 to 70 mole percent of maleic



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anhydride and 30 to 70 mole percent of acrylamide or methacrylamide.

16. A copolymer as claimed in claim 14 consisting of 45 to 55 mole percent maleic anhydride and 45 to 55 mole percent acrylamide.

17. A process for preparing a copolymer as claimed in claim 14 which comprises:

5 heating a mixture of (a) said maleic anhydride and (b) said acrylamide or methacrylamide in the appropriate proportions in a chain transfer solvent mixture to at least 120°C, introducing from 2 to 20 weight percent based on the total weight of the monomers of a free radical initiator and continuing to maintain said mixture at a temperature of at least 120°C until polymerisation is essentially complete, said chain transfer solvent mixture being (i) 10 from 15 to 85 weight percent of an aromatic solvent selected from mono and dialkyl substituted benzenes having from 1 to 4 carbon atoms in each alkyl group and trialkyl substituted benzenes having 1 to 2 carbon atoms in each alkyl group, and (ii) from 15 to 85 weight percent of a ketone solvent selected from dialkyl ketones having from 1 to 5 carbon atoms in each alkyl group, the alkyl groups being the same or different, and cycloalkanones 15 having from 5 to 8 carbon atoms in the cycloalkyl group.

18. A process of claim 17 which includes the steps of isolating said copolymer after polymerization and treating said polymer with water at a temperature below 30°C to remove any unreacted monomer.

19. A process as claimed in claim 17 or 18 wherein the copolymer prepared consists of 20 30 to 70 mole percent of maleic anhydride and 30 to 70 mole percent of acrylamide or methacrylamide.

20. A process as claimed in claim 17 or 18 wherein the copolymer prepared consists of 45 to 55 mole percent maleic anhydride and 45 to 55 mole percent acrylamide.

21. A process as claimed in any one of claims 17 to 20 wherein said chain transfer solvent mixture component (i) is xylene and component (ii) is methyl isobutyl ketone or 4-methyl-2-pentanone.

22. A process as claimed in any one of claims 17 to 21 wherein said mixture is maintained at a temperature of from 125°C to 150°C until polymerization is substantially complete and wherein said free radical initiator is di-*t*-butyl peroxide.

23. A method for the prevention of scale formation when heating or desalinating water containing scale forming impurities, which comprises mixing with said water the hydrolyzed form of a terpolymer or an alkali metal, amine or ammonium salt thereof as claimed in any one of claims 1 to 8, at a concentration of at least 2 parts per million.

24. A method as claimed in claim 23 wherein the terpolymer consists of 41 to 45 mole percent maleic anhydride, 45 to 49 mole percent acrylamide and 9 to 13 mole percent styrene.

25. A process as claimed in claim 9 substantially as hereinbefore described in any one of Examples 1 to 7.

26. A process as claimed in claim 17 substantially as hereinbefore described in any one of Examples 8 to 10.

27. A terpolymer as claimed in claim 1 which has been prepared by a process as claimed in any one of claims 9 to 13 and 25.

28. A copolymer as claimed in claim 14 which has been prepared by a process as claimed in any one of claims 17 to 22 and 26.

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