# PATENT SPECIFICATION

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## (54) IMPROVEMENTS IN OR RELATING TO PHASE-REVERSIBLE COMPOSITIONS CONTAINING POLYMERIC ANIONS

(71) We, NIPPON OIL COMPANY LIMITED, a Japanese Company of No. 3—12, Nishi-Shinbashi 1-chome, Minato-ku, Tokyo, Japan, 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:—

The present invention relates to phase-reversible compositions for use in the manufacture of adhesives, fire-extinguishing agents, viscosity control agents, tackifiers, coating agents, dye assistants, and the like. The compositions of the invention are phase-reversible between liquid at a low temperature and solid at a higher temperature.

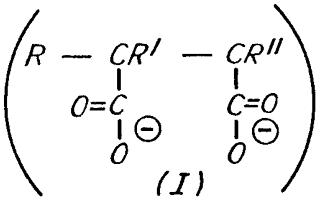
Known examples of such phase-reversible compositions are methylcellulose and polyoxyethylene, both being liquid at a low temperature due to hydration of their hydrophilic radicals and solid at elevated temperature due to destruction of the hydration structures. These high molecular weight materials have a common drawback in that they tend to release free water when changing into a solid phase at increased temperature, and hence a prolonged period of time is required to bring them back into a liquid state similar to that which existed prior to the heating.

In order to eliminate or reduce the above-mentioned drawback of the previously known compositions, the present Applicants have already developed certain improved compositions which are disclosed in their co-pending U.K. Patent Application No. 1,525,004. These compositions essentially comprise (1) high-molecular weight anions resulting from the partial or complete dissociation of the carboxylic group of a conjugated dienemaleic acid derivative copolymer, (2) alkali metal or quaternary ammonium cations, (3) magnesium ions, (4) anions combinable with $Mg^{2+}$ to form a water-soluble magnesium compound, and (5) water. The compositions of the co-pending Application are reversible between liquid and solid at an increased speed and in addition are extremely easy to control as regards their viscosity at low temperature and their gel strength at high temperature. For these advantages, the prior compositions of the present Applicants have been found useful in the preparation of fire-extinguishing agents, textile printing materials, glues, viscosity-control agents, water-soluble quenching media and the like. However, it was later found that the prior compositions are not completely satisfactory so far as their compatibility with other water-soluble organic materials is concerned, and, moreover, their surface-active properties, such as foaming ability, dispersability and emulsifiability, are rather poor.

It is an object of the present invention to provide improved compositions which are phase-reversible between liquid and solid and which have a good compatibility with other water-soluble organic materials and a high surface-activity.

In accordance with the present invention, there is provided a phase-reversible composition comprising:

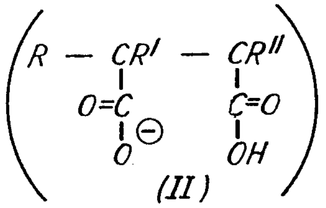
(A) a high-molecular weight anion resulting from the dissociation of at least a part of the carboxylic groups of a conjugated diene-maleic acid or maleic acid derivative copolymer having repeating units of the formulae:



$$\left(\begin{array}{ccc} R\ - & CR'\ - & CR'' \\ & | & | \\ & O=C & C=O \\ & |\ominus & |\ominus \\ & O & O \end{array}\right)$$

(I)

and/or



$$\left(\begin{array}{ccc} R\ - & CR'\ - & CR'' \\ & | & | \\ & O=C & C=O \\ & |\ominus & | \\ & O & OH \end{array}\right)$$

(II)

where R is a conjugated diene unit in the copolymer and each of R′ and R″ is hydrogen, a halogen atom, or an organic radical having from 1 to 18 carbon atoms; and terminal radicals of the formula

$$R'''\text{—}Y\text{—} \qquad \text{(III)}$$

where R‴ is an organic radical having from 4 to 30 carbon atoms; and Y is —S— or —$SO_2$—;

(B) one or more of the cations $Na^+$, $K^+$, $Li^+$ and quaternary ammonium cations of the formula

$$R_1R_2R_3R_4N^+ \qquad \text{(IV)}$$

where $R_1$, $R_2$, $R_3$, and $R_4$ are hydrogen, an alkyl radical of from 1 to 18 carbon atoms, a cycloalkyl radical or a phenyl radical and may be the same or different, said cations being present in an amount of 0.5 to 5.0 equivalents based on the maleic acid or maleic acid derivative unit in the component (A);

(C) $Mg^{2+}$ in an amount of 0.5 to 2.0 equivalents based on the maleic acid or maleic acid derivative unit in the component (A);

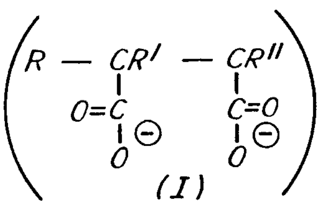
(D) an anion $X^{n-}$ (where n is 1 or 2) which is combinable with $Mg^{2+}$ to form a water-soluble magnesium compound, said anion being present in an amount of from 0.5 to 7.0 equivalents based on the maleic acid or maleic acid derivative unit in the component (A); and

(E) water in an amount from 1 to 1000 times the total weight of the components (A), (B), (C) and (D).

The essential difference between the compositions of the present invention and those of our co-pending Application No. 1,525,004, lies in the provision of the sulphur-containing terminal radicals represented by R‴—Y—; such terminal radicals are not present in the compositions of the earlier Application.

Each of the components (A) to (D) will now be described in greater detail.

Component (A) is a high-molecular anion resulting from the dissociation of at least a part of the carboxylic groups of a conjugated diene-maleic acid or maleic acid derivative copolymer having repeating units of the formulae



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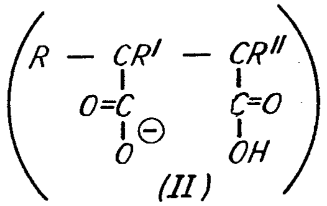
and/or



$$\left(\begin{array}{ccc} R\ - & CR'\ - & CR'' \\ & | & | \\ & O=C & C=O \\ & |\ominus & | \\ & O & OH \end{array}\right)$$

(II)

where R is a conjugated diene unit in the copolymer; and R′ and R″ are each hydrogen, a halogen atom or an organic radical having from 1 to 18 carbon atoms. The degree of dissociation when represented in terms of the ratio of I:II is in the range of from 100:0 to 0:100, preferably from 100:0 to 50:50.

Component (A) also has terminal radicals represented by R‴—Y—, as defined above. Conjugated dienes used in the preparation of the starting conjugated diene-maleic acid or maleic acid derivative may be aliphatic or cyclic compounds of 4—20 carbon atoms with conjugated ethylenic double bonds including, for example, butadiene, isoprene, chloroprene, 2,3-dimethylbutadiene, 2,3-dichlorobutadiene, piperilene, 2-methyl, 1,3-hexadiene, or 1-methoxy, 1,3-butadiene. The maleic acid or derivative unit may be maleic acid, chlormaleic acid, dichlormaleic acid, or citraconic acid. The R‴— portion of the terminal radical is an organic radical having a carbon number of from 4 to 30, preferably from 6 to 20. Examples of such

R'''— radicals are primary straight-chain alkyl radicals such as 1-butyl, 1-pentyl, 1-hexyl, 1-heptyl, 1-octyl, 1-nonyl, 1-decyl, 1-dodecyl, 1-tetradecyl, 1-hexadecyl, 1-octadecyl and 1-eicocyl radicals. The R'''— radical may alternatively be a primary, secondary or tertiary alkyl radical having its hydrogen atoms substituted by other alkyl radicals or organic residues to an extent such that the number of carbon atoms of the total radicals does not exceed 30. As such R'''— radicals, there may be used aryl or substituted aryl radicals such as phenyl, ortho, meta- and para-toluyl, alpha-toluyl, alpha- and beta-naphthyl; aryl-alkyl radicals such as phenylbutyl, phenylpentyl, phenylhexyl, phenyloctyl, phenylnonyl, phenyldecyl, phenyldodecyl, phenyltetradecyl, phenylhexadecyl, phenyloctadecyl; and cycloalkyl radicals such as cyclohexyl, cyclooctyl and cyclododecyl radicals. The terminal radicals are usually present in amounts of from 0.5 to 30% by weight of the polymer, preferably from 1.0 to 20% by weight. Less than 0.5 weight percent fails to exhibit the desired function of the terminal radicals, whilst more than 30 weight percent necessarily results in a reduced molecular weight, and hence reduced polymeric characteristics.

The conjugated diene-maleic acid or maleic acid derivative copolymer which is a starting material for component (A) may be prepared by a polymerisation process, for example, using free-radical generating catalysts, ultraviolet rays, ionisation radiant rays or organometallic catalysts. An important aspect of the invention resides in the incorporation into the conjugated diene-maleic acid or maleic acid derivative copolymer of such terminal radicals as have been defined above. This may be accomplished, for example by introducing a sulphur-containing compound into the polymerisation system, such compound being a thiol or a disulphide which is known for its high capability of chain transfer to the polymer. The copolymer thereby obtained possesses an R'''S-terminal radical. The type of mercaptan or disulphide to be used depends upon the type of terminal radical desired and, in some cases, should be chosen in relation to the molecular weight of a particular starting copolymer. Typical examples of thiols and disulphides which can be used are compounds having 4 to 30, preferably 6 to 20, carbon atoms, such as 2 - methyl - 2 - propane - thiol, 1-butanethiol, 2-butanethiol, 1,1,3,3 - tetramethyl - butanethiol, 1-pentanethiol, 1-hexanethiol, 2-hexanethiol, 1,1,3,3 - tetramethyl - 1 - hexanethiol, 1,1,3,3,5,5 - hexamethyl - 1 - hexanethiol, 1-heptanethiol, 1-decanethiol, 1-octanethiol, 1,1,3,3,5,5,7,7 - octamethyl - 1 - octanethiol, 1-dodecanethiol, 1-tetradecanethiol, 1-octadecanethiol, benzenethiol, p-chlorobenzenethiol, o-toluenethiol, m-toluenethiol, p-toluenethiol, α-toluenethiol, 1-naphthalenethiol, phenyldodecanethiol, phenyloctanethiol, cyclohexanethiol, butylsulphide, butyldisulphide, benzoyldisulphide, bis(p-chlorobenzoyl)disulphide dodecylsulphide and mixture of two or more of these. The amount of these materials will depend on the molecular weight of the starting copolymer used, and is generally in the range of 0.5 to 60% by weight, preferably 1.0 to 30% by weight of the total monomer.

As previously stated, in the preparation of the conjugated diene-maleic acid copolymer, free-radical-generating catalysts may be employed, examples of such catalysts being azo-compounds and peroxides. The catalysts are used together with the sulphur-containing compounds required to produce the terminal radicals. Other known processes may be resorted to for the introduction of $R'''—SO_2—$ radicals.

It has now been found that the excellent properties of the compositions in accordance with the invention including phase-reversibility, compatibility and surface-activity are all attributable to an oleophilic radical introduced at the terminal of a high-molecular anion which forms a part of the component (A). The Y-portion of the R'''—Y-radical serves as a bridge between the oleophilic terminal radical and a hydrophilic polymer portion.

The conjugated diene employed in the invention may be, for example, butadiene, isoprene, chloroprene, 2,3-dimethylbutadiene, 2,3-dichlorobutadiene, piperylene, 2 - methyl - 1,3 - hexadiene, or 1 - methoxy - 1,3 - butadiene. The maleic acid derivative used may be maleic acid, maleic acid anhydride, chlormaleic acid anhydride, chlormaleic acid, dichlormaleic acid, citraconic acid anhydride, a maleic monoalkylester, or a maleic dialkylester.

The conjugated diene-maleic acid or maleic acid derivative copolymer having the above-specified terminal radicals is subjected to reaction with a base in water, whereby a high-molecular anion is formed as the component (A). This reaction progresses very satisfactorily where the maleic acid derivative unit in the copolymer is maleic acid, maleic acid anhydride, or citraconic acid. If the derivative unit is a maleic monoalkylester or a maleic dialkylester, the base also functions as a hydrolysis catalyst and there can therefore eventually be obtained the desired high-molecular anion of the component (A). The anion may also be obtained by hydrolysis of a maleic monoalkyl or dialkyl ester in the presence of an acid catalyst, followed by the addition of a predetermined amount of a base.

Conjugated diene-maleic acid or maleic acid derivative copolymers used as a starting material for the component (A) should preferably have an intrinsic viscosity of the order of 0.01 to 2.0, preferably 0.1 to 1.0, as measured in different solvents at 30°C. The composition ratio of conjugated diene units to maleic acid or derivative units can be determined by NMR spectrum or potassium hydroxide titration. Generally, most such conjugated diene-maleic acid or maleic acid derivative copolymers are a 1:1 alternate copolymer.

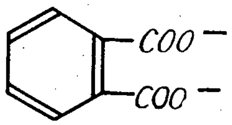
The component (B) is constituted by one or more of the alkali metal cations $Na^+$, $K^+$ and $Li^+$, or quaternary ammonium cations of the formula $R_1R_2\overset{+}{N}R_3R_4$. When the reaction of the conjugated diene-maleic acid derivative copolymer with a base is carried out in water in order to attain the desired degree of dissociation of the high-molecular anion in the component (A), the component (B) may be incorporated as the counter-cation for the high-molecular anion. The component (B) is preferably used in amounts of from 0.5 to 5.0 equivalents, more preferably from 0.8 to 2.0 equivalents, based on the maleic acid or derivative unit in the component (A). As used herein, the term "equivalent" means that one gram ion corresponds to one mole of the maleic acid unit, irrespective of the electrical charge of the ion. This is accomplished by preparing the anion of the component (A) having a predetermined degree of dissociation, using a base of an equivalent mole or two-fold mole of the maleic acid derivative unit in the starting conjugated diene-maleic acid or maleic acid derivative copolymer. The progress of this reaction may be observed by the IR spectrum. So long as the desired degree of dissociation is maintained in the component (A), neutral compounds such as salts, for example, sodium chloride and sodium sulphate, may be added for other purposes. However, in such a case, $Na^+$ tends to increase in the composition; the total amount of the component (B) including this should therefore be in the range of from 0.5 to 5.0 equivalents.

The base used for reaction with the conjugated diene-maleic acid or maleic acid derivative copolymer may be an alkali metal compound, including sodium hydroxide, potassium hydroxide, lithium hydroxide, sodium carbonate, potassium carbonate, and lithium carbonate, or an amine including ammonia, a primary amine such as methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, sec-butylamine, tert-butylamine, n-hexylamine, n-octylamine, laurylamine, cyclohexylamine, aniline and benzylamine, a secondary amine such as dimethylamine, diethylamine, methylethylamine, dipropylamine, diisopropylamine, dibutylamine, diphenylamine, N-methylaniline, N-methylcyclohexylamine, pyrrolidine, piperidine and morpholine, a tertiary amine such as trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, dimethylhexylamine, tri-n-octylamine, pyridine, dimethylaniline, N-methylpyrrolidine, N-methyl-piperidine and N-methylmorpholine, or a quaternary ammonium hydroxide such as tetramethyl ammonium hydroxide. Either a single one of these or a mixture thereof may be used. The nature of the component (B) depends upon the nature of the base or bases employed and the amount of the former compared with the total amount of the latter. However, depending upon the type of process hereafter described used for preparing the compositions, the amount of the component (B) in the phase-reversible composition may not always correspond to the amount of the base used but is often less due to partial removal during the separating operation. Therefore, the amount of the component (B) should be considered as such which is present in the final composition.

Component (C) of the phase-reversible composition according to the present invention is the magnesium ion $Mg^{2+}$. The $Mg^{2+}$ plays an important role in producing the characteristics of the composition, that it is liquid at low temperature, becomes solid with increasing temperature and returns to its initial liquid state on cooling. The $Mg^{2+}$ may be in the form of a water-soluble magnesium-containing compound, usually a magnesium salt. It is preferable to use a magnesium compound which is readily soluble in water with a view to providing $Mg^{2+}$ ions with ease during the preparation of the phase-reversible composition. Examples of such magnesium compounds include magnesium salts of mineral acids, such as magnesium chloride, magnesium permanganate and magnesium sulphate, and magnesium salts of organic acids, such as magnesium acetate, magnesium propionate, magnesium formate and magnesium phthalate, as well as mixtures thereof. Any other magnesium compound which is convertible into a water-soluble one to provide $Mg^{2+}$ ions, may also be employed.

Preferred amounts of $Mg^{2+}$ ions are in the range from 0.3 to 2.0, more preferably from 0.5 to 1.5, equivalents based on the maleic acid or derivative unit in the conjugated diene-maleic acid or maleic acid derivative copolymer of the component (A). The amount of $Mg^{2+}$ ions should always be determined on the basis of $Mg^{2+}$ ions present in the final composition.

Component (D) is an anion of the formula $X^{n-}$, where n is 1 or 2. The $X^{n-}$ is an anion which combines with $Mg^{2+}$ to form a water-soluble magnesium compound or an anion residue resulting from the magnesium compound used in the preparation of the phase-reversible composition after liberating $Mg^{2+}$. They may be inorganic anions, such as for example, $Cl^-$, $Br^-$, $MnO_4^-$, $NO_3^-$, $ClO_4^-$ and $SO_4^{2-}$, or organic carboxylate anions such as $HCOO^-$, $CH_3COO^-$, $CH_3CH_2COO^-$ and



When alkali metal compounds such as their carbonates and hydrogen carbonates are employed as the base for reaction with the conjugated diene-maleic acid or maleic acid derivative copolymer, resulting from the dissociation in water of $Na^+$, $K^+$ or $Li^+$, there will be available anion residues such as, for example, $HCO_3^-$, which are also applicable as $X^{n-}$. Accordingly, the amount of the component (D) corresponds to the amount of $Mg^{2+}$ present, and when carbonates or hydrogen carbonates are used, varies in dependence upon the amount of $N_a^+$, $K^+$ or $Li^+$. Anion residues available from compounds added for other purposes, such as, for example, sodium chloride and sodium hydroxide may also be used. The total amount of the $X^{n-}$ anions is in the range of from 0.5 to 7.0, preferably from 0.7 to 3.5 equivalents based on the maleic acid or derivative unit in the component (A). There may be $OH^-$ ions.

Finally, there is the component (E), i.e. water, which is essential for the preparation of the phase-reversible composition. The various ions in the composition are present in water at low temperature either independently of one another or in weak interaction, the entire composition being liquid; whereas the interaction is enhanced with an increase in temperature to a cross-linked state, thereby forming a solid with water contained therein. When the solidified composition is cooled, it will again be liquid to recover fluidity. The amount of water is from 1 to 1000 times, preferably from 2 to 500 times the total amount of components (A), (B), (C) and (D), and should be determined in dependence upon the viscosity in the liquid state and the strength in the solid state which are desired for a particular application of the final composition.

The composition when heated is solid and may vary from a jelly-like to a rubber-like state, depending upon the quantitative relations of the components (A), (B), (C), (D) and (E) respectively.

It has now been found that the absence of any one of the above components or departures from the specified relative amounts of the individual will fail to produce the desired composition of the invention.

A process for preparing the compositions according to the invention will now be described. A conjugated diene-maleic acid or maleic acid derivative copolymer of the class described having terminal radicals of the formula R‴—Y—, and a predetermined amount of an alkali metal or ammonium compound, or an amine or mixture thereof, are mixed in water and reacted with stirring at a temperature ranging from room temperature to the boiling point of the water. The pH of the solution of the aqueous alkali metal salt or amine salt of the conjugated diene-maleic acid or maleic acid derivative copolymer in this reaction should be in the range of from 7 to 14, preferably from 7 to 12. A lower pH than 7 will fail to produce the intended results of the invention, even with addition of a magnesium compound in the process step hereinafter described.

A predetermined amount of a magnesium compound is added to the resulting aqueous solution after cooling. When the magnesium compound is used in an amount corresponding to 0.5—0.8 equivalent of $Mg^{2+}$ based on the maleic acid or derivative unit, with a starting copolymer having an intrinsic viscosity of 0.6, the resulting solution will be a phase-reversible composition according to the invention. The solution when heated to a temperature above about 80°C, changes into a jelly-like solid, and when cooled, returns to the initial liquid state; thus, the composition undergoes a reversible change between a liquid and a solid phase.

When the magnesium compound is added in an amount corresponding to 0.8—2.5 equivalents of $Mg^{2+}$ based on the maleic acid or derivative unit, the solution becomes cloudy and on being held still undergoes liquid-liquid phase separation into a low-viscosity upper layer and a high-viscosity lower layer. The lower layer when heated, gradually becomes solidified with an increase in temperature from about 60°C, and turns into a strong rubbery, elastic solid at 80°C or above. When the solid is cooled, it will then gradually be liquefied and will return finally to the initial liquid state. Atomic absorption spectrum analysis shows that the lower layer does not contain the whole amount of $Mg^{2+}$ ions formed from the magnesium compound used, but that a portion of the $Mg^{2+}$ ions remains in the upper layer at the time of two-layer separation.

With the magnesium compound added in an amount corresponding to 0.8—2.5 equivalents of $Mg^{2+}$ based on the maleic acid or derivative unit, the whole solution is heated with stirring, without undergoing the two-layer separation, until a solid mass is precipitated in the solution. It is separated by filtration while hot and cooled to give a liquid, which, when heated, becomes a rubbery solid. The composition of the mass is the same as that of the lower-layer solution obtained by the two-layer separation. The two compositions are identical.

If the composition that will become a rubbery solid on heating is diluted with water, the strength of the solid is reduced finally to give a jelly-like solid. It should thus be noted that the two compositions, one exhibiting a jelly-like tendency and the other exhibiting a rubber-like tendency when heated, are substantially identical and both are phase-reversible compositions according to the invention. This indicates that adjustment of the amount of $Mg^{2+}$ ions in the composition allows a change of the properties of the solid obtained on heating, and this is one of the distinguishing features of the invention.

If, for instance, the composition is found to be deficient in the amount of the component (B), namely alkali metal cations or quaternary ammonium ions, it will suffice to simply add a required amount of alkali metal compound or amine, followed by thorough stirring, thereby providing a phase-reversible composition according to the invention.

As an alternative process for the preparation of a composition according to the invention, there may be mentioned a process which comprises feeding predetermined amounts of a conjugated diene-maleic acid or maleic acid derivative copolymer, a base such as alkali metal compound or an amine, a magnesium compound and water all together into a reactor and heating the mixture with stirring, whereby there may be obtained the desired phase-reversible composition. When the composition thus obtained is taken up with a large amount of a hydrophilic solvent, such as methanol or acetone, to form precipitates which are separated by filtration and dried *in vacuo*, a hard glass-like solid can be obtained. Evaporation of the water directly from the composition gives a solid plate or film. These solids are convenient to handle during storage or transportation and can be converted to the desired composition, when it is to be used, by adding a predetermined amount of water and thoroughly stirring them to form a homogeneous liquid.

In addition to the property of the phase-reversible composition of the invention that it is reversibly changeable in its phase between liquid and solid as discussed above, the compositions of the invention have excellent compatibility and high surface-activity. These additional features may be attributed to the oleophilic radicals which are introduced at the end of the high-molecular anion in the component (A). The oliophilic radicals function to form a hydrophobic bond with other organic substances, thereby enhancing the solubility of the latter. When the high-molecular anions of the component (A) are taken as a whole, the anion portion of the conjugated diene-maleic acid or maleic acid derivative copolymer is hydrophilic and the terminal radicals are hydrophobic, which leads to an excellent surface-activity in the final composition. For these features of the invention, the phase-revesible compositions may find wide application in commerce, such as, for example, an adhesive compound, a fire-fighting agent, a viscosity-control agent, a tackifier, a coating agent, a dye assistant, and the like. When applied as a foam-type fire-fighting agent, the compositions of the invention exhibit excellent foaming ability due to their surface-activity. The foams generated will increase in their strength with increasing temperature when the composition is exposed to flames. In order to increase the quantity of foam to be generated, a surface-active agent may be added, and the amount of such additive may be adjusted at will since the phase-reversible composition of the invention is highly compatible.

The compositions of the invention are also highly miscible with or dispersible in a wide variety of dyes and textile printing agents. Moreover, when heated as in the usual dye treatment, the phase-reversible composition can make use of its gelation properties for effectively setting the dye. Conversely, it may be utilised as a resist glue since the composition can readily return to a liquid state on cooling.

The invention is illustrated by the following examples:—

### Comparative Example 1

To a 3-litre autoclave equipped with a stirrer and a gas-intake tube, and purged with nitrogen gas, there were charged 2,500 ml of acetone, 294 g maleic acid anhydride and 4.9 g azo-bis-isobutyronitrile. Reaction was effected at 70°C with 162 g butadiene added slowly over a period of 4 hours. The reaction product was introduced in small droplets into large amounts of benzene to precipitate a polymer. The resulting polymer was filtrated, washed with benzene and dried *in vacuo* for 50 hours, thereby obtaining 300 g refined polymer. The intrinsic viscosity of this polymer was 0.64 when determined in cyclohexanone at 30°C. (These measuring conditions were the same throughout the following examples). Nuclear Magnetic Resonance (NMR) spectrum analysis indicated that terminal radicals in the copolymer were not great enough to be quantitative determined. 15.2 g of the polymer was charged into a 300 ml separating flask equipped with a stirrer and a reflux condenser, followed by the addition of 155 g water and 7.2 g sodium hydroxide. The mixture was heated with stirring for 2 hours until a transparent solution was obtained. To this solution, after cooling, was added 90 ml of magnesium chloride solution of 1 mol/litre concentration, and the mixture stirred vigorously and held still overnight, until the solution had separated into two layers. The viscous lower layer was separated. This liquid composition changed into a rubber-like solid when heated to a temperature of 70°C or above and returned to its initial liquid state when cooled to room temperature or below. The liquid composition here obtained will hereinafter be referred to as C-1.

### Example 1

The same apparatus and method as was used in Comparative Example 1 were employed for the reaction of 2,500 ml of acetone, 294 g maleic anhydride, 162 g butadiene, 4.9 g azo-bis-isobutylnitrile and 18.0 g of n-dodecyl-mercaptan. There was obtained 278 g of a butadiene-maleic acid anhydride copolymer. The viscosity of this polymer was 0.21. Its sulphur content was 0.33%. Terminal dodecylthio radicals as calculated from the sulphur content were 2.2% of the polymer, corresponding well to an NMR value of 2.3. 15.5 g of polymer was charged to a separation flask of the type used in Comparative Example 1, followed by the addition of 155 g water and 10.7 g potassium hydroxide. The whole was stirred at room temperature for 4 hours. To the solution thereby obtained was added 130 ml of a mol/litre solution of magnesium sulphate and the mixture stirred vigorously. It was then heated for 2 hours using a heating bath at 100°C but without stirring, whereupon the solution separated into a rubber-like solid phase and a liquid phase, respectively. The liquid layer was removed and thereafter the flask was cooled, whereby the rubbery solid became progressively liquefied. After the lapse of one hour, a viscous transparent liquid was obtained. This will hereinafter be referred to as E-1.

### Example 2

A separation flask of 500 cc. capacity was charged with 15.5 g of the polymer of Example 1, 20.2 g of triethylamine, 12.9 g of magnesium acetate $4H_2O$ and 200 g water. The charge was stirred for 4 hours at room temperature, until there was obtained a transparent, homogeneous solution. A portion of this solution was transferred to a test tube and heated until it lost its fluidity and turned into a jelly. This jelly-like product returned to its initial liquid state when cooled. It is referred to as E-2.

### Example 3

10 g of the composition E-1 obtained in Example 1 was admixed with 190 g water. The resulting solution was checked for its foaming ability, revealing an

expansion ratio of 3.0 by the Weeks method. This showed satisfactory surface-activity for the composition E-1.

### Example 4

The procedure of Comparative Example 1 was followed in the reaction of 204 g of isoprene, 294 g maleic acid anhydride, 4.9 g azo-bis-isobutylnitrile, 30.0 g of n-butylmercaptan and 2,500 ml of acetone. There was obtained 340 g of isoprene-maleic anhydride copolymer. This polymer had an intrinsic viscosity of 0.11, and butylthio radicals were present therein in an amount of 3.5% as determined by sulphur analysis and the NMR spectrum. 17.2 g of polymer was charged to a 500-ml separable flask, followed by the addition of 12.3 g potassium hydroxide and 300 g water. The whole was heated with stirring for 2 hours until it was liquefied. To the liquid, after being cooled, was added 60 ml of a 1 mol/litre solution of magnesium chloride and the mixture stirred. The liquid composition thereby obtained was heated at 90°C, when it turned into a jelly, and reversely cooled to room temperature, when it returned to its initial liquid state. This composition is referred to as E-4. 1.0 g of this composition was admixed with 1.5 g of C.I. Disperse Orange 13, B-3E, and 50 g of water, thereby obtaining a dye solution. At the same time, 1.0 g of composition C-1 was admixed with 1.5 g of Dyanics Orange B-3E and 50 g of water, to prepare a second dye solution. The two dye solutions were compared for dispersability. The former was well dispersed even after a period of 12 consecutive hours, while the latter precipitated after a period of 2 hours.

### Example 5

The procedure of Comparative Example 1 was followed in reacting 162 g of butadiene, 336 g of citraconic acid anhydride, 20 g paratoluenethiol, 15.9 g of laurylperoxide and 2,500 ml of cyclohexanone. There was obtained 240 g of a butadiene-citraconic anhydride copolymer, which had an intrinsic viscosity of 0.19, and paratoluylthio and lauryl radicals in an amount of 6.7% of the total polymer. 17.7 g of polymer, 7.1 g of lithium hydroxide $1H_2O$ solution and 400 g water were charged to a 500-ml separating flask and heated with stirring for 2 hours. The whole, after being cooled, was further mixed with 70 ml of 1 mol/litre magnesium acetate solution and stirred for 1 hour. A portion of the resulting liquid was sampled and heated, whereupon it turned into a jelly-like solid. This solid returned to its initial liquid state when recooled. The composition is referred to as E-5.

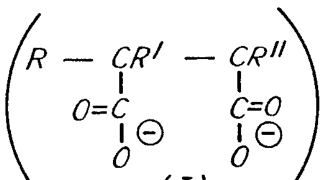
TABLE 1

| | | Composition | | | | |
|---|---|---|---|---|---|---|
| | | A | B | C | D | E |
| Example No. | I:II | Maleic Acid Derivative Unit | Equivalent | Equivalent | Equivalent | E/A+B+C+D (Wt. Ratio) |
| 1 | 9:1 | 1 | 0.91 | 1.00 | 0.52 | 4.3 |
| 2 | 10:0 | 1 | 2.00 | 0.60 | 1.20 | 4.5 |
| 4 | 10:0 | 1 | 2.20 | 0.60 | 1.20 | 10.2 |
| 5 | 7:3 | 1 | 1.70 | 0.70 | 1.40 | 14.1 |

WHAT WE CLAIM IS:—

1. A phase-reversible composition comprising:

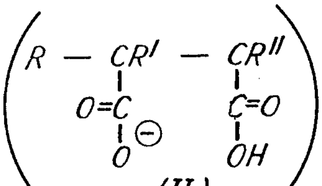
(A) a high-molecular weight anion resulting from the dissociation of at least a part of the carboxylic groups of a conjugated diene-maleic acid or maleic acid derivative copolymer having repeating units of the formulae:



$$\left( R - \underset{\underset{\underset{O^{\ominus}}{|}}{O=C}}{\underset{|}{CR'}} - \underset{\underset{\underset{O^{\ominus}}{|}}{C=O}}{\underset{|}{CR''}} \right)$$

(I)

and/or



$$\left( R - \underset{\underset{\underset{O^{\ominus}}{|}}{O=C}}{\underset{|}{CR'}} - \underset{\underset{\underset{OH}{|}}{C=O}}{\underset{|}{CR''}} \right)$$

(II)

where R is a conjugated diene unit in the copolymer and each of R′ and R″ is hydrogen, a halogen atom, or an organic radical having from 1 to 18 carbon atoms; and terminal radicals of the formula

$$R'''—Y— \qquad (III)$$

where R''' is an organic radical having from 4 to 30 carbon atoms; and Y is —S— or —$SO_2$—;

(B) one or more of the cations $Na^+$, $K^+$, $Li^+$ and quaternary ammonium cations of the formula

$$R_1R_2R_3R_4N^+ \qquad (IV)$$

where $R_1$, $R_2$, $R_3$ and $R_4$ are hydrogen, an alkyl radical of from 1 to 18 carbon atoms, a cycloalkyl radical or a phenyl radical and may be the same or different, said cations being present in an amount of 0.5 to 5.0 equivalents based on the maleic acid or maleic acid derivative unit in the component (A);

(C) $Mg^{2+}$ in an amount of from 0.5 to 2.0 equivalents based on the maleic acid or maleic acid derivative unit in the component (A);

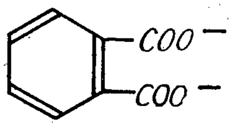
(D) an anion $X^{n-}$ (where n is 1 or 2) which is combinable with $Mg^{2+}$ to form a water-soluble magnesium compound, said anion being present in an amount of from 0.5 to 7.0 equivalents based on the maleic acid or maleic acid derivative unit in the component (A); and

(E) water in an amount of from 1 to 1000 times the total weight of the components (A), (B), (C) and (D).

2. A composition as claimed in Claim 1, wherein said conjugated diene unit is butadiene, isoprene, chloroprene, 2,3-dimethylbutadiene, 2,3-dichlorobutadiene, piperilene, 2-methyl-1,3-hexadiene, 2,4-hexadiene, or 1-methoxy-1,3-butadiene.

3. A composition as claimed in Claim 1 or Claim 2, wherein said maleic acid or maleic acid derivative unit is maleic acid, chloromaleic acid, or citraconic acid.

4. A composition as claimed in any one of Claims 1 to 3, wherein said anion $X^{n-}$ is $Cl^-$, $Br^-$, $SO_4^{2-}$, $MnO_4^-$, $NO_3^-$, $ClO_4^-$, $HCOO^-$, $CH_3COO^-$, $CH_3CH_2COO^-$, or



5. A composition as claimed in any one of the preceding Claims, wherein the amount of said terminal radicals is in the range of from 0.5 to 30% by weight of said copolymer.

6. A composition as claimed in any one of the preceding Claims, wherein said conjugated diene-maleic acid or maleic acid derivative copolymer has an intrinsic viscosity of from 0.01 to 2.0.

7. A phase-reversible composition substantially as hereinbefore described with reference to any of Examples 1 to 5.

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