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(57) Abstract

The invention provides water repellent compositions comprising a wax and a styrene (meth)acrylic copolymer comprising at least some active hydrogen; water resistant objects such as gypsum objects comprising the water repellent compositions and processes for forming water resistance objects using the water repellent compositions.

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WATER REPELLENT COMPOSITIONS, PROCESSES AND APPLICATIONS THEREFOR

BRIEF SUMMARY OF THE INVENTION

This invention relates to water repellent compositions and objects which have been treated with said water repellent compositions. This invention also relates to a process for producing a water repellent composition, a process for imparting water resistance to an object and a process for producing a water resistant object. This invention also relates to objects and applications utilising said compositions and processes.

BACKGROUND OF THE INVENTION

Water repellent compositions are useful for imparting water resistance to a variety of objects. In particular, these objects include panels and blocks used in the building industry. The panels and blocks used in the building industry include gypsum board, plaster board, wall board, gypsum fibreboard, large hollow-core wall panels, bricks, blocks and the like. However, it will be appreciated that water repellent compositions are also useful for a wide variety of objects including foodstuffs, cosmetics, packaging materials and other items.

In particular, the aforesaid panels and blocks suffer from the disadvantage that upon water absorption there is a loss of desired properties such as strength, fire retardancy, sound shielding properties, etc.

In particular, building panels and blocks such as plasterboard, gypsum board or wallboard as it is otherwise known, gypsum fibreboard, hollow-core panels and blocks are produced by the reaction of anhydrous calcium sulphate or calcium sulphate hemihydrate with water and allowing the mixture to hydrate or set as calcium sulphate dihydrate which is relatively hard.

Building panels such as plasterboard, gypsum board or wallboard usually are formed from a core of set gypsum which is positioned between a pair of outer liners which form the respective outer faces of the building panel. The pair of outer liners are generally made from paper or fibreglass.

Gypsum fibreboard is formed from a core of set gypsum which contains a fibrous reinforcement of randomly dispersed cellulosic or glass fibres or the like. The gypsum core may be positioned on one liner of paper or fibreglass, or positioned between two liners, or cast on a belt without any liners whatsoever, in which case the set gypsum composition forms the surfaces of the finished panel.

Large scale hollow-core panels are formed from a core of set gypsum which may or may not contain fibrous reinforcement, and may or may not be cast on a liner or positioned between two liners. The panel is cast in a mould with hollow tubes positioned in it that are removed after the gypsum has set. These large scale hollow-core panels are

commonly used as structural load-bearing wall components for internal and external walls.

Bricks and blocks are formed from set gypsum which may contain cellulosic or fibreglass reinforcement or the like. The bricks or blocks are cast in moulds.

In use, these building panels and blocks are commonly exposed to water and since set gypsum readily absorbs water, such water absorption leads to the deleterious effect mentioned previously, i.e. loss of strength, fire retardancy, etc.

Whilst there are water repellent compositions known to coat such products, it has been surprisingly discovered that the use of the water repellent composition of this invention provides enhanced water resistance to objects. Further, the use of the water repellent composition of this invention can lead to the benefit of increased throughput of production of building panels which are water resistant since less water may be required in the formation of the panel.

This invention seeks to ameliorate the disadvantages of the known water repellent compositions by imparting improved water resistance, or at least provide a useful alternative.

SUMMARY OF THE INVENTION

According to a first embodiment of this invention, there is provided a water repellent composition comprising:

a) a wax; and

b) a styrene (meth)acrylic copolymer comprising at least some active hydrogen.

According to a second embodiment of this invention, there is provided a water repellent composition comprising:

a) a wax;

b) a styrene (meth)acrylic copolymer comprising at least some active hydrogen; and

c) a protective colloid compound.

The water repellent composition of the first or second embodiment may further comprise

d) an alkaline compound.

In particular, according to a third embodiment of this invention, there is provided a water repellent composition comprising:

a) a wax;

b) a styrene (meth)acrylic copolymer comprising at least some active hydrogen;

c) a protective colloid compound; and

d) an alkaline compound.

According to a fourth embodiment of this invention, there is provided a water repellent composition comprising:

a) a wax;

b) a styrene (meth)acrylic copolymer comprising at least some active hydrogen;

c) a polyvinyl alcohol having a saponification degree of at least 75 mol %; and

d) an alkaline compound.

The water repellent compositions of the invention may further comprise

e) a hydrocarbon resin.

In particular, according to a fifth embodiment of this invention, there is provided a water repellent composition comprising:

a) a wax;

b) a styrene (meth)acrylic copolymer comprising at least some active hydrogen;

c) a polyvinyl alcohol having a saponification degree of at least 75 mol %;

d) an alkaline compound; and

e) a hydrocarbon resin.

According to a sixth embodiment of this invention, there is provided a water resistant object comprising an object and the water repellent composition according to any one of the first to fifth embodiments of this invention.

According to a seventh embodiment of this invention, there is provided a water resistant gypsum composition comprising gypsum and the water repellent composition according to any one of the first to fifth embodiments of this invention.

According to an eighth embodiment of this invention, there is provided a shaped object comprising the water repellent composition according to any one of the first to fifth embodiments of this invention.

According to a ninth embodiment of this invention, there is provided a panel comprising the water repellent composition of any one of the first to fifth embodiments of this invention.

According to a tenth embodiment of this invention, there is provided a panel comprising the water repellent composition of any one of the first to fifth embodiments of this invention wherein the panel is plasterboard, gypsum board, wallboard, gypsum fibreboard, large hollow-core gypsum panel or the like.

According to an eleventh embodiment of this invention, there is provided a layered product comprising:

i) at least one liner; and

ii) a water resistant set gypsum comprising the water repellent composition of any one of the first to fifth embodiments of this invention.

According to a twelfth embodiment of this invention, there is provided a layered product comprising:

i) a first liner and a second liner;

ii) a water resistant set gypsum comprising the water repellent composition of any one of the first to fifth embodiments of this invention positioned such that the water resistant gypsum is between the first liner and the second liner.

According to a thirteenth embodiment of this invention, there is provided a panel comprising the layered product of either the eleventh or twelfth embodiments of this invention.

According to a fourteenth embodiment of this invention, there is provided a plasterboard comprising the layered product of the eleventh or twelfth embodiments of this invention.

According to a fifteenth embodiment of this invention, there is provided a process for forming a water resistant object comprising the steps of applying a water repellent composition according to any one of the first to fifth embodiments of this invention to an object.

According to a sixteenth embodiment of this invention, there is provided a process for forming a water resistant panel comprising the steps of applying a water repellent composition according to any one of the first to fifth embodiments of this invention to a panel.

According to a seventeenth embodiment of this invention, there is provided a process for forming a water resistant plasterboard, gypsum board or the like comprising the steps of applying the water repellent composition according to any one of the first to fifth embodiments of this invention to a plasterboard, gypsum board or the like.

According to an eighteenth embodiment of this invention, there is provided a process for producing a gypsum plasterboard comprising the steps of

(i) forming a stucco slurry from gypsum rock; and

(ii) adding a water repellent composition of any one of the first to fifth embodiments of this invention to the stucco slurry to form a treated stucco slurry; and

(iii) forming a gypsum plasterboard from the treated stucco slurry.

According to a nineteenth embodiment of this invention, there is provided a water resistant object formed from applying the water repellent composition of any one of the first to fifth embodiments of this invention to an object.

Typically a surfactant is added as a further component to the composition of any one of the first to fifth embodiments of this invention.

DETAILED DESCRIPTION OF THE INVENTION

Throughout this specification, unless the context clearly indicates otherwise, the words "comprise", "comprises", "comprising" or other variations thereof shall be understood as meaning that the stated integer is included and does not exclude other integers from being present even though those other integers are not explicitly stated.

As used herein, the expression "styrene (meth)acrylic acid copolymer" refers to copolymers which predominantly comprise copolymerised styrene and acrylic acid and/or methacrylic acid, and includes within its meaning such copolymers which include other comonomers and/or in which the carboxyl groups of the acrylic or methacrylic acid residues

are partially esterified. Thus the styrene (meth)acrylic copolymer includes at least some free carboxyl groups and therefore includes at least some active hydrogen.

As used herein, the expression "water resistant" refers to an object which has been treated so that when contacted with water the object does not degrade as rapidly as would the same object which had not been so treated.

Typically, the component a) wax in the water repellent composition is a paraffin wax, slack wax, polyolefin wax, ozokerite wax, ceresin wax. Still typically, the wax has a melting point in the range of 40 to 90° Celsius. Still more typically, the wax is a paraffin wax or polyolefin wax. The wax acts as a primary waterproofing agent in the water repellent composition. The component a) wax may also be a mixture of two or more of the aforesaid types of waxes.

Typically, the component b) styrene (meth)acrylic copolymer comprising at least some active hydrogen in the water repellent composition is a copolymer of styrene and acrylic acid or methacrylic acid. The acrylic acid or methacrylic acid may be partially esterified. The esterification of the styrene (meth)acrylic acid copolymer is achieved by use of fatty acid alcohols, typically C_1-C_{15} fatty acid alcohols.

Typically, the weight average molecular weight of the styrene (meth)acrylic acid copolymer is 500 to 100,000, still more typically 1000 to 90,000, 1500 to 50,000, 1500 to 30,000, 1500 to 20,000, or 1500 to 10,000 and more typically 1800 to 8500.

Typically, the styrene (meth)acrylic acid copolymer is in its salt form.

The styrene (meth)acrylic acid copolymer acts as a dispersing agent which provides better dispersion in the water repellent composition. The styrene (meth)acrylic acid copolymer typically forms a substantially insoluble water impervious film on an object thereby imparting water resistance to the object. Typically, in applications utilising panels such as gypsum board, wall board and plaster board, the styrene (meth)acrylic acid copolymer also enhances the bonding of liner papers to the core of the panel. The use of styrene (meth)acrylic acid copolymer is compatible with other dispersants and additives used in water repellent compositions.

Examples of alkali soluble, acid containing copolymers useful as the styrene (meth)acrylic acid copolymer in the compositions of this invention are: styrene-acrylic acid copolymers, styrene-methacrylic acid copolymers, styrene-acrylonitrile-acrylic acid copolymers, styrene-butyl acrylate-acrylic acid copolymers, and the like. The styrene may be partially replaced with other hydrophobic monomers such as alpha-methylstyrene; alkyl substituted styrenes such as vinyl toluene; acrylonitrile; vinyl chloride; acrylic- and methacrylic esters, such as butyl acrylate, methyl methacrylate and the like, or mixtures thereof; vinyl esters, such as vinyl acetate or vinyl laurate; fumarate esters, such as dibutyl fumarate; itaconate esters, such as dibutyl itaconate; olefins, such as ethylene, and the like, or mixtures thereof. In place of part of the acrylic or methacrylic acid, other copolymerizable, unsaturated acids may be used in the synthesis of styrene (meth)acrylic acid copolymer. Examples of such copolymerisable unsaturated acids are crotonic acid,

itaconic acid and the like. Unsaturated sulfonic acids, such as vinyl sulfonic acid or styrene sulfonic acid and the like may also be used.

The acid number of the styrene (meth)acrylic acid copolymer is at least 100 and generally from 100 to 400, preferably from 190 to 250. When a styrene-acrylic acid copolymer is used in the compositions of this invention the weight ratio of styrene to acrylic acid is generally from about 6:1 to about 1.5:1, preferably from about 5:1 to about 2.5:1. The styrene (meth)acrylic acid copolymer can be any of the commercially available products, such as Morez 101, sold by Morton Chemical Company, or Flexbond 25, sold by the Air Products Co., or Joncryl 678 sold by S. C. Johnson Company. Some of these commercial copolymers are available as aqueous solutions and can be used in the compositions of the invention as such. If they are in a solid form they have to be dissolved in an alkaline medium at elevated temperature. Alkali compounds such as ammonium hydroxide, sodium hydroxide, potassium hydroxide, soda ash and the like, as well as water soluble mono-, di- and trialkyl- or hydroxyalkyl amines, such as methyl or ethyl amine or monoethanolamine, may be employed to solubilize the styrene (meth)acrylic acid copolymer. The pH of the solution of the styrene (meth)acrylic acid copolymer is generally about from 6 to 10, preferably from about 7.5 to 9. The aqueous styrene (meth)acrylic acid copolymer solution generally has a solids level of from 20 to 40% w/v.

Typically, the water repellent composition further comprises other additives such as dispersing agents, emulsifiers, buffers, surfactants, wetting agents, thickeners, etc. Typically, the dispersant is selected from the group such as lignosulphonates and aldehyde based dispersants. Suitable buffering agents include potassium carbonate, sodium carbonate and lithium carbonate. Suitable surfactants include sulfonated petroleum derivatives and their salts, sulfonated carboxylic acids and their salts, ethylene oxide modified surfactants, and fluorine modified surfactants.

Typically, the water repellent composition further comprises one or more wetting agents selected from fluorine modified wetting agents, silicon containing wetting agents and ethylene oxide modified wetting agents.

Typically, the water repellent composition further comprises one or more thickeners selected from natural or modified gums, methyl, ethyl or propyl cellulose, hydroxyethylcellulose and hydroxypropyl cellulose.

Typically, the component c) protective colloid compound in the composition of the second and third embodiments is a polyvinyl alcohol, a natural or modified gum. The polyvinyl alcohol is more typically a partially or fully hydrolysed alcohol, still more typically in the range of 75 to 100% hydrolysed. The typical viscosity of the polyvinyl alcohol is 3 to 50 centipoise when tested as a 4% aqueous dispersion.

Typically, the component d) alkaline compound in the composition of the third, fourth and fifth embodiments is a water soluble compound and is selected from the group of alkali metal hydroxides such as lithium hydroxide, sodium hydroxide and potassium hydroxide; alkali metal carbonates such as sodium carbonate and potassium carbonate;

ammonia; ammonium hydroxide; amines such as dimethylamine, trimethylamine and triethylamine; and ethanolamines such as triethanolamine, diethanolamine, dimethylethanolamine and methyldiethanolamine. Typically, the alkaline compound is added in an amount of from 0.3 to 3 times the amount required for neutralising the styrene (meth)acrylic acid copolymer.

Typically, the component e) hydrocarbon resin in the composition of the fifth embodiment is a petroleum resin such as a coumarone-indene resin having a molecular weight of from 500 to 3000 obtainable by polymerising a C_9 aromatic hydrocarbon or C_5 aliphatic hydrocarbon fraction obtained from the refinery of petroleum or from a process of a petroleum chemical industry, by way of a Friedel-Crafts catalyst; a terpene resin having a molecular weight of from 500 to 3000 obtainable from turpentine oil; rosin; a homopolymer or copolymer of ethylene, propylene, butene, isobutylene or styrene having a molecular weight of from 500 to 30 000 and a melting point of at least 95° C, or asphalt. The hydrocarbon resins used in the present invention may also includes other atoms such as oxygen.

The weight percent of component a) wax in respect of the total weight of components a) to e) of the water repellent compositions is:

typically 20 to 99.5 percent by weight,

more typically 25 to 99.5 percent by weight,

still more typically 30 to 95 percent by weight,

even more typically 35 to 90 percent by weight,

yet more typically 40 to 85 percent by weight.

The following Table A provides typical weight ratios of the component a) wax to the component b) styrene (meth)acrylic copolymer in the water repellent composition of this invention.

Table A

Wax (parts by weight)	Styrene (meth)acrylic copolymer containing at least some active hydrogen (parts by weight)
1	0.005, 0.006, 0.007, 0.008, 0.009, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.15, 0.20, 0.25, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.0, 1.1, 1.2

Typically, the weight ratio of the component a) wax to the component b) styrene (meth)acrylic copolymer of this invention is selected within the range of from 1 to 0.005 to 1 to 0.3, more typically 1 to 0.005 to 1 to 0.2, still more typically 1 to 0.01 to 1 to 0.1.

The weight percentage range of component b) styrene (meth)acrylic acid copolymer in respect of the total weight of components a) to e) of the water repellent compositions is:

typically 0.5 to 60 percent by weight,

more typically 0.5 to 50 percent by weight,
still more typically 0.5 to 40 percent by weight,
even more typically 0.5 to 30 percent by weight,
yet more typically 0.5 to 20 percent by weight,
most typically 1.0 to 10 percent by weight.

The weight percentage range of component c) protective colloid compound, when present, in respect of the total weight components a) to e) of the water repellent compositions is:

typically 0.1 to 20 percent by weight,
more typically 0.5 to 15 percent by weight,
still more typically 0.75 to 10 percent by weight,
even more typically 0.75 to 7.5 percent by weight
yet more typically 1.0 to 5 percent by weight.

The weight percentage range of component d) alkaline compound, when present, in respect of components a) to e) of the total weight of the water repellent compositions is

typically 0 to 10 percent by weight,
more typically 0.1 to 10 percent by weight,
still more typically 0.1 to 7.5 percent by weight,
even more typically 0.1 to 5.0 percent by weight.

The weight percentage range of component e) hydrocarbon resin, when present, in respect of the total weight of components a) to e) of the water repellent compositions is

typically 0 to 10 percent by weight,
more typically 0.1 to 10 percent by weight,
still more typically 0.5 to 7.5 percent by weight,
even more typically 0.5 to 5.0 percent by weight,

and yet more typically is dependent upon the required water resistance for the desired object to be treated with the water repellent composition.

Typically, further compatible waxes, polymers, resins and additives may be added to the water repellent composition to achieve desired properties as may be envisaged for various types of objects. More typically, a water soluble polymer such as a polyacrylamide, methylcellulose, carboxymethylcellulose, hydroxyethylcellulose or hydroxypropylcellulose may be incorporated into the water repellent composition.

In an illustrative process for preparing one water repellent composition of the invention, paraffin wax with a melting point between 40°C and 90°C is heated in a tank to 120°C and a petroleum resin with a softening point of 95 to 100°C is dissolved in it. In a second tank, polyvinyl alcohol is dispersed in water and heated to 95°C to dissolve it. A solution of styrene acrylic resin dissolved in water with the aid of an alkaline compound is added to the polyvinyl alcohol solution, together with such other additives as may be required to impart further desirable properties to the emulsion to be formed. Preferred styrene acrylic resins are commercially available as JONCRYL 678 or JONCRYL 682 (S.

C. Johnson & Co.) or MOREZ 100 or MOREZ 101 (Morton Polymers) The water solution containing polyvinyl alcohol and styrene acrylic resin, and the wax solution containing petroleum resin are combined to form an emulsion with the aid of suitable emulsification equipment.

Typical processes for production of the water repellent composition comprise phase reversal emulsification or mechanical emulsification. These methods may be used alone or in combination. The mechanical emulsification may be conducted by a homomixer, a valve homogeniser, a colloid mill or a supersonic method, or any other suitable method.

The water repellent composition is useful for improving the water resistance of objects including fibres, papers, cardboard, wood materials or synthetic wood materials (particle boards and fibreboards); cosmetics; aggregate materials such as concrete, gravel or the like; and foodstuffs such as fruit, particularly apples. Typically, the water repellent composition is used for plasterboard, wallboard or gypsum board, gypsum fibreboard, large scale hollow-core gypsum panels, and gypsum bricks and blocks.

In the processes of the fifteenth, sixteenth, seventeenth and nineteenth embodiments of the present invention the step of applying the water repellent composition may involve any convenient application method. For example, the application may be by spraying, rolling, brushing, dipping or curtain coating. If desired, selected areas of objects such as panels may have the water repellent composition applied to them by printing techniques such as transfer rolling or screen printing.

Typically, the water repellent composition is an aqueous emulsion and a sufficient amount of water is added to the components a), b) and c) to e) when present, as required for the particular application required. Usually, the ratio of the weight of water to the total weight of components a) to e) is about 1:1 but this may be varied to suit the desired application. Typically, suitable solubilisers to effect the solution of the styrene (meth)acrylic copolymer for use in the emulsion include alkali metal or ammonium hydroxides and are typically employed in an amount of 0.05 to 10%, by weight, of the emulsion.

The following Table B provides a typical blend proportion of gypsum to the water repellent composition of any one of the first to fifth embodiments, in a water resistant gypsum composition of the seventh embodiment of this invention. Table B illustrates for entries numbered 1-24 the blend proportion of gypsum:water repellent composition in parts by weight.

Table B

Entry	Gypsum (parts by weight)	Water Repellent Composition (parts by weight)
1	10	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
2	9.80	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
3	9.75	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
4	9.50	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
5	9.25	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
6	9.0	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
7	8.75	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
8	8.50	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
9	8.25	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
10	8.00	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
11	7.75	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
12	7.50	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
13	7.25	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
14	7.00	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
15	6.75	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
16	6.50	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
17	6	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.

18	5.75	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
19	5.5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
20	5	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
21	4	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5, 1.75, 2.0.
22	3	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0, 1.25, 1.5.
23	2	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 1.0.
24	1	0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5.

Typically, gypsum is added to a water repellent composition of this invention comprising the following components:

a) a wax having a melting point of 40 to 90° C;

b) a styrene (meth)acrylic acid copolymer;

c) a protective colloid compound; and

d) an alkaline compound.

More typically e) a hydrocarbon resin is also added.

Typically, the gypsum is added in an amount of 50 to 99.5% by weight, more typically 60 to 99.5% by weight, still more typically 70 to 99.5% by weight, even more typically 80 to 99.5% by weight, yet more typically 90 to 99.5% by weight, most typically 92 to 95% by weight, based on the total weight of gypsum and water repellent composition.

Gypsum compositions of this invention are settable by hydration to form a water resistant gypsum product. Typically the gypsum product is gypsum plaster, plasterboard, wall board, gypsum fibreboard, large hollow-core gypsum panel, gypsum brick or block, or the like.

Typically, gypsum is selected from naturally occurring forms of calcium sulphate, flue gas desulphurisation plant wastes, phosphoric acid manufacturing wastes, hydrochloric acid manufacturing wastes etc. More typically the gypsum is extracted from mines or quarry as gypsum rock. Still more typically the gypsum rock is crushed, blended with gypsumboard waste and then is screened. During the crushing process, or after crushing and screening, the gypsum is dried by suitable means such as passing heated air through the crushing mill, or drying in a rotating kiln or oven so as to evaporate any surface moisture on the gypsum. Dry gypsum is ground by crushers or rollers to form a desired particulate size of gypsum.

Usually, the dried gypsum is then calcined by suitable means to remove chemically combined water, and so form gypsum hemihydrate.

Generally, the gypsum hemihydrate is mixed with water, a water repellent composition of this invention, and such other additives as may be required, to form a gypsum slurry. The gypsum slurry so formed is then placed in a mould or positioned in a layered product.

Typically, the settable gypsum composition is set so as to form a set gypsum product which is water resistant and layered with at least one liner to form a layered product. Typically, the water resistant gypsum is positioned in a layered product comprising:

a) a first liner;

b) the water resistant gypsum;

c) a second liner.

The layered product may be formed into a shaped product most typically a panel. Accordingly, there is also provided a panel comprising:

a) a first liner;

b) the water resistant gypsum according to this invention; and

c) a second liner.

Typically, the water resistant gypsum is sandwiched between the first and second liners so as to form a layered product and more typically a panel such as plasterboard, wallboard or the like. Typically, the first and second liners may be selected from paper, fibreglass, wood, laminates or other materials commonly used in layered products. The shaped products such as panels are useful in the construction industry as building panels such as walls, ceilings, etc.

Thus, in another form of this invention, there is provided a method of forming a layered product comprising the steps of:

(i) forming a layer of a water resistant gypsum which has been treated with the water repellent composition according to any one of the first to fifth embodiments of this invention on a first liner;

(ii) disposing a second liner on the water resistant gypsum so that the first liner is in an opposed relationship to the second liner and whereby the water resistant gypsum is positioned between the first and second liners; and

(iii) drying said layered product so as to allow hydration of the gypsum.

Typically, the layered product is formed into a shaped product. More typically, the layered product is formed into a panel. Still more typically, the layered product is formed into a board especially adapted for the construction industry.

Typically, the formation of a panel incorporating the water resistant gypsum comprises the following steps:

a) mixing gypsum rock with or without recycled plasterboard;

b) crushing and screening the mixture of gypsum rock and plaster board;

c) drying the gypsum rock and plasterboard to remove excess water;

d) calcining the gypsum to form gypsum hemihydrate;

e) mixing the water repellent composition of any one of the first to fifth embodiments of this invention with water to form a dispersion; and

f) mixing the gypsum hemihydrate and the dispersion from step (e) to form a stucco slurry;

g) spreading the slurry between liner papers;

h) allowing the slurry to set to form a panel; and

i) kiln drying the panel.

Still typically, further additives may also be incorporated in the dispersion of step e) to provide further strength, fire retardancy, ease of manufacture etc.

Advantages in the production of wet area gypsum plasterboard containing the water repellent composition of this invention may include reduced water requirement to obtain a stucco slurry of suitable consistency, improved bond of the set gypsum core to the liner papers covering said core, reduced drier temperatures, reduced energy costs, improved board quality due to reduced end-burn of boards during drying.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graphical representation of comparative water absorption over periods of two hours and twenty four hours in 2.5 centimetre cube specimens of set gypsum composition containing either Emulsion A or Emulsion D described in the following Preparation Examples, or one of two commercially available wax emulsion waterproofing compounds.

Figure 2 is a graphical representation of comparative water absorption in 2.5 centimetre cube specimens of set gypsum composition containing Emulsion A described in the following Preparation Examples or a commercially available wax emulsion waterproofing compound.

Figure 3 is a graphical representation of comparative water absorption in 2.5 centimetre cube specimens of set gypsum composition containing Emulsion D described in the following Preparation Examples or either of two commercially available wax emulsion waterproofing compounds (Freemulsion 754 and Rhenium).

EXAMPLES

This invention will now be described, by way of illustration only, with reference to the following examples. The examples should not be construed as limiting the generality of the above description.

Preparation Example 1

One hundred and ninety six parts of paraffin wax having a melting point of 58°C and 22 parts of a C_9 aromatic petroleum resin with a softening point of 98°C and a bromine value of 30 were melted at 130°C and the temperature was lowered to 120°C. Separately, 12 parts of polyvinyl alcohol with a saponification degree of 89% were dispersed in 222 parts of water and heated to 95°C. To this was added a solution comprised of 4 parts styrene

acrylic resin with a molecular weight of 8700 and an acid number of 215, and 1 part of potassium hydroxide, both dissolved in 15 parts of water. The wax and water solutions were combined in a closed dispersion mixer and the mixture was emulsified by passing it through a piston type pressure homogeniser at 1050 psi (7300kPa). The emulsified mixture was then cooled to obtain an emulsion **A** with a solids content of 50%.

Preparation Example 2

An emulsion having a solids content of 50% was prepared in the same manner as in Preparation Example 1, except that 2.5 parts of potassium carbonate were added to the water phase prior to combining the wax and water phases to obtain an emulsion **B**.

Preparation Example 3

An emulsion having a solids content of 50% was prepared in the same manner as in Preparation Example 2, except that 1 part of a proprietary diphenol oxide sulfonate solution AEROSOL DPOS-45 (Cytec) was added to the water phase prior to combining the wax and water phases to obtain an emulsion **C**.

Preparation Example 4

An emulsion having a solids content of 50% was prepared in the same manner as in Preparation Example 1, except 22 parts of a mixed C_9 aromatic/C_5 aliphatic petroleum resin with a softening point of 97°C were dissolved in the wax phase instead of the C_9 aromatic petroleum resin to obtain an emulsion **D**.

Water Absorption

The quantity of water required to prepare a gypsum slurry of normal consistency was determined. Gypsum slurries were prepared using various emulsion waterproofing additives at 5% of the dry stucco weight mixed with a suitable amount of water to give the same ratios of total liquid to dry stucco, and 25 millimetre cube specimens were cast from the prepared slurries. The cubes were dried in an oven at 180°C until they had reached 75% of their initial mass, and then dried at 45°C for 20 hours. The dried weight of the specimens was recorded, and they were immersed in water at 23°C. After 2 hours, the specimens were reweighed, and the water absorption was determined. The results are shown in table C. The gypsum hemihydrate used to prepare the specimens was from a gypsum plasterboard plant in New Zealand.

2 Hr WATER ABSORPTION		
EMULSION	**DOSE RATE**	**ABSORPTION**
EMULSION A	5%	0.6%
FREEMULSION 759	5%	2.2%
DIAPROOF GX	5%	0.7%

Table C

A similar experiment was conducted in which 2.5 cm cubes cast from gypsum slurries, containing Emulsion A or Emulsion D as described in the above Preparation Examples or containing Freemulsion 754 or Freemulsion 759, were dried as described above and immersed in water for 24 hours. In each case amount of waterproofing additive was 5% by weight based on the weight of dry stucco. The water absorption of the immersed cube was measured after 2 and 24 hours and the results are set out in Table D below and are plotted in Figure 1.

	Percent (w/w) water absorption after:	
	2 hours	24 hours
Freemulsion 754	1.0	8.6
Freemulsion 759	1.1	11.1
Emulsion D	0.8	1.5
Emulsion A	0.8	1.4

Table D

Figure 2 is a graphical representation of comparative water absorption, over a period of up to 72 hours, in 2.5 centimetre cube specimens of set gypsum composition containing Emulsion A described in the Preparation Examples or Freemulsion 754. Both emulsions were dosed at the rated of 8.3% by weight of dry stucco. The results are set out in Table E.

	Percent (w/w) water absorption after:			
	2 hours	24 hours	48 hours	72 hours
Freemulsion 754	2.1	9.2	10.8	12.8
Emulsion A	1.0	3.1	4.1	4.8

Table E

Freemulsions 754 and 759 are proprietary wax emulsion waterproofing additives for plasterboard marketed by PCA Hodgson Chemicals. Diaproof is a proprietary wax emulsion waterproofing additive produced by Mitsubishi Chemical Corporation, and disclosed in Japanese Patent Application Number JP 42164/89 dated February 22, 1989, and subsequent European Patent Application number EP 0 384 322 A1 filed February 16, 1990, and United States Patent number 5,098,943 dated March 24, 1992.

Figure 3 is a graphical representation of comparative water absorption in 2.5 centimetre cube specimens of set gypsum composition containing Emulsion D described in the Preparation Examples or either of two commercially available wax emulsion waterproofing compounds (Freemulsion 754 and Rhenium, a proprietary wax emulsion

waterproofing additive produced by Rhenium Co.) The results are set out in Table F. The waterproofing additives were added in amounts of 5%, 7.5% or 10% by weight of the dry stucco, as indicated.

Treatment	Waterproofing additive	Percent (w/w) water absorption after:			
		2 hours	24 hours	48 hours	72 hours
1	Freemulsion 754 at 5%	6.6	20.0	21.2	22.6
2	Freemulsion 754 at 7.5%	2.7	10.4	11.8	12.0
3	Freemulsion 754 at 10%	2.0	4.2	5.3	5.6
4	Emulsion D at 5%	1.9	3.9	5.0	5.8
5	Emulsion D at 7.5%	2.3	3.6	4.2	4.9
6	Emulsion D at 10%	2.3	3.9	4.9	5.4
7	Rhenium at 5%	9.0	33.8	22.3	35.3
8	Rhenium at 7.5%	4.8	15.6	10.1	17.3
9	Rhenium at 10%	4.5	7.8	10.6	15.1

Table F

Dispersion

Emulsion based waterproofing additives tend to thicken gypsum slurries, increasing the quantity of water required in the mix to achieve normal consistency. This excess water must be removed in the drying process, and increases the porosity of the finished plasterboard. The dispersing effect observed with waterproofing emulsions prepared according to this invention reduces the quantity of water required to produce a gypsum slurry of normal consistency.

The water required to prepare a gypsum slurry of normal consistency was determined by hand mixing gypsum hemihydrate powder with water. The prepared slurry was poured into a cylindrical mould 35 millimetres in diameter with a height of 51 millimetres. The mould was lifted one minute from the addition of the gypsum hemihydrate powder to the water, and the diameter of the resulting pat of gypsum slurry was measured. Normal consistency was defined as the quantity of water required to produce a pat of 100 ± 3 millimetres in diameter.

Gypsum slurries were prepared using emulsion based waterproofing additives mixed with the water to give the same total liquid content as had been previously determined to yield a slurry of normal consistency. The diameter of the gypsum paste resulting from these slurries indicates the dispersing effect of emulsions prepared according to this invention. The results are shown in Table G. The gypsum hemihydrate used was obtained from a gypsum plasterboard plant in Chile.

DISPERSION			
EMULSION	**DOSE RATE**	**TOTAL LIQUID**	**DIAMETER**
Blank		59g	100m
EMULSION A	5%	59g	109mm
FREEMULSION 754	5%	59g	65mm

Table G

Stucco slurry incorporating the Wax/Styrene acrylic Emulsion has increased fluidity when compared to stucco slurry without the emulsion, or when compared to stucco slurry containing a commercially available waterproofing wax emulsion. The increased fluidity will allow production of wet area gypsum plasterboard with reduced water content, improved production efficiencies such as faster line speed and reduced end-burn of boards in the drying kiln, and reduced energy costs in the drying kiln due to the lower drying temperature required to remove the excess water from the gypsum plasterboard.

Similar slurries were prepared by the same method using gypsum hemihydrate from Australian sources. The wax emulsions were added at a dose rate of 5% by weight of the dry stucco in each case. The results are shown in Table H.

DISPERSION		
	AUSTRALIAN STUCCO	
	STUCCO 1	**STUCCO 2**
BLANK	100mm	100mm
EMULSION A	120mm	103mm
EMULSION B	117mm	
EMULSION C	123mm	116mm
EMULSION D	120mm	
EMULSION D	112mm	
FREEMULSION 754	68mm	
FREEMULSION 754		73mm

Table H

Stucco slurries containing emulsions made with styrene acrylic Resin (Emulsions A to D) clearly show an increase in dispersion when compared to those containing a commercially available proprietary wax emulsion waterproofing compound, or when compared to stucco slurries containing no wax emulsion. The stucco slurries will require

less water to attain a suitable consistency for plasterboard production, and hence the plasterboard will require less energy to dry.

Production of Gypsum Wallboard

A preferred aspect of this water repellent composition is to form water resistant gypsum plasterboard or wallboard. The following description of an example illustrates a typical method of producing wallboard or plasterboard which is water resistant.

a) Gypsum rock is extracted from a suitable source for example a mine or a quarry. The extracted gypsum rock is then transported to a plant where the gypsum rock is inserted into crushers, blended with reclaimed wasteboard and screened to a suitable size typically no more than 5cm in diameter.

b) After crushing and screening, the gypsum rock is dried by suitable means such as a rotating kiln or oven which evaporates the surface moisture from the gypsum rock.

c) Once the gypsum rock is dried the gypsum is ground by suitable means such as rollers.

d) Plaster is calcined or heated to remove excess water which is chemically bonded to the gypsum in a kettle calciner or flash calciner to form stucco.

e) Once the stucco is formed it is suitably mixed with other desired additives such as pearlite, starch, fibreglass or vermiculite so as to provide a range of properties, for example, fire retardancy, sound proofing, etc.

f) Water is then added together with the water repellent composition as described in any one of the Preparation Examples 1 to 4 above, and soap foam and accelerators in a mixing vessel at the beginning of a board forming line after suitable mixing.

g) The resulting slurry is disposed between two paper sheets which also act as a mould.

h) The stucco slurry is sandwiched between the two paper sheets and allowed to set so as to form the water resistant gypsum layer between the two outer sheets or liners.

i) The resulting layered product is formed into a long continuous sheet or wallboard and placed on a conveyor and roller where it is cut after the stucco slurry has hardened.

j) The cut boards are subjected to further drying and heating in a multi-stage kiln.

k) The resulting wallboard is then ready for transportation.

Modifications and variations such as would be apparent to a skilled addressee are deemed to be within the scope of this invention. It is also understood that the scope of this invention should not be limited to the examples or drawings illustrated above.

CLAIMS

1. A water repellent composition comprising:
   a) a wax; and
   b) a styrene (meth)acrylic copolymer comprising at least some active hydrogen.

2. A water repellent composition comprising:
   a) a wax;
   b) a styrene (meth)acrylic copolymer comprising at least some active hydrogen; and
   c) a protective colloid compound.

3. A water repellent composition comprising:
   a) a wax;
   b) a styrene (meth)acrylic copolymer comprising at least some active hydrogen;
   c) a protective colloid compound; and
   d) an alkaline compound.

4. A water repellent composition comprising:
   a) a wax;
   b) a styrene (meth)acrylic copolymer comprising at least some active hydrogen;
   c) a polyvinyl alcohol having a saponification degree of at least 75 mol %; and
   d) an alkaline compound.

5. A water repellent composition comprising:
   a) a wax;
   b) a styrene (meth)acrylic copolymer comprising at least some active hydrogen;
   c) a polyvinyl alcohol having a saponification degree of at least 75 mol %;
   d) an alkaline compound; and
   e) a hydrocarbon resin.

6. A water repellent composition according to any one of claims 1 to 5 wherein said wax has a melting point of 40 to 90°C.

7. A water repellent composition according to any one of claims 1 to 5, wherein said styrene (meth)acrylic copolymer is selected from the group consisting of styrene-acrylic acid copolymers, styrene-methacrylic acid copolymers, styrene-acrylonitrile-acrylic acid copolymers, styrene-butyl acrylate-acrylic acid copolymers and partially esterified derivatives thereof.

8. A water repellent composition according to any one of claims 1 to 5 wherein said wax is selected from the group consisting of paraffin wax, slack wax, polyolefin wax, ozokerite wax and ceresin wax.

9. A water resistant object comprising an object and a water repellent composition according to claim 1.

10. A water resistant gypsum composition comprising gypsum and a water repellent composition according to claim 1.

11. A panel comprising a water resistant gypsum composition of claim 10.

12. A layered product comprising:

i) at least one liner; and

ii) a water resistant set gypsum comprising the water repellent composition of claim 1.

13. A panel comprising the layered product of claim 12.

14. A plasterboard comprising the layered product of claim 12.

15. A process for forming a water resistant object comprising the step of applying a water repellent composition according to claim 1 to the object.

16. A process for forming a water resistant panel comprising the step of applying a water repellent composition according to claim 1 to the panel.

17. A process for forming a water resistant plasterboard, gypsum board or the like comprising the steps of applying the water repellent composition according to claim 1 to the plasterboard, gypsum board or the like.

18. A process for producing a gypsum plasterboard comprising the steps of

(i) forming a stucco slurry from gypsum rock;

(ii) adding a water repellent composition of claim 1 to the stucco slurry to form a treated stucco slurry; and

(iii) forming a gypsum plasterboard from the treated stucco slurry.

19. A water resistant object formed from applying the water repellent composition of claim 1 to an object.

20. A process for forming a layered product comprising the steps of:

(i) forming a layer of a water resistant gypsum composition according to claim 10 on a first liner;

(ii) disposing a second liner on the water resistant gypsum composition so that the first liner is in an opposed relationship to the second liner and whereby the water resistant gypsum composition is positioned between the first and second liners; and

(iii) drying said layered product so as to allow hydration of the gypsum.

AMENDED CLAIMS

[received by the International Bureau on 10 August 2000 (10.08.00);
original claims 1-10, 12 and 15-19 amended; remaining claims unchanged (2 pages)]

1. A water repellent aqueous emulsion composition comprising:

a) a wax: and

b) an aqueous solution of a salt of a styrene (meth)acrylic copolymer comprising at least some active hydrogen.

2. A water repellent aqueous emulsion composition comprising:

a) a wax:

b) an aqueous solution of a salt of a styrene (meth)acrylic copolymer comprising at least some active hydrogen: and

c) a protective colloid compound.

3. A water repellent aqueous emulsion composition comprising:

a) a wax:

b) an aqueous solution of a salt of a styrene (meth)acrylic copolymer comprising at least some active hydrogen:

c) a protective colloid compound: and

d) an alkaline compound.

4. A water repellent aqueous emulsion composition comprising:

a) a wax:

b) an aqueous solution of a salt of a styrene (meth)acrylic copolymer comprising at least some active hydrogen:

c) a polyvinyl alcohol having a saponification degree of at least 75 mol %: and

d) an alkaline compound.

5. A water repellent aqueous emulsion composition comprising:

a) a wax:

b) an aqueous solution of a salt of a styrene (meth)acrylic copolymer comprising at least some active hydrogen:

c) a polyvinyl alcohol having a saponification degree of at least 75 mol %:

d) an alkaline compound: and

e) a hydrocarbon resin.

6. A composition according to any one of claims 1 to 5, wherein said wax has a melting point of 40 to 90°C.

7. A composition according to any one of claims 1 to 5, wherein said styrene (meth)acrylic copolymer is selected from the group consisting of styrene-acrylic acid copolymers, styrene-methacrylic acid copolymers, styrene-acrylonitrile-acrylic acid copolymers, styrene-butyl acrylate-acrylic acid copolymers and partially esterified derivatives thereof.

8. A composition according to any one of claims 1 to 5 wherein said wax is selected from the group consisting of paraffin wax, slack wax, polyolefin wax, ozokerite wax and ceresin wax.

9. A water resistant object comprising an object and a composition according to claim 1.

10. A water resistant gypsum composition comprising gypsum and a composition according to claim 1.

11. A panel comprising a water resistant gypsum composition of claim 10.

12. A layered product comprising:

i) at least one liner; and

ii) a water resistant set gypsum comprising a composition according to claim 1.

13. A panel comprising the layered product of claim 12.

14. A plasterboard comprising the layered product of claim 12.

15. A process for forming a gypsum product comprising mixing gypsum hemihydrate with water and a composition according to claim 1 to form a gypsum slurry, placing said gypsum slurry into a mould or in a layered product and setting said gypsum slurry to form said gypsum product.

16. A process for forming a water resistant panel comprising the step of applying a composition according to claim 1 to the panel.

17. A process for forming a water resistant plasterboard, gypsum board or the like comprising the steps of applying a composition according to claim 1 to the plasterboard, gypsum board or the like.

18. A process for producing a gypsum plasterboard comprising the steps of

(i) forming a stucco slurry from gypsum rock;

(ii) adding a composition according to claim 1 to the stucco slurry to form a treated stucco slurry; and

(iii) forming a gypsum plasterboard from the treated stucco slurry.

19. A water resistant object formed from applying the composition of claim 1 to an object.

20. A process for forming a layered product comprising the steps of:

(i) forming a layer of a water resistant gypsum composition according to claim 10 on a first liner;

(ii) disposing a second liner on the water resistant gypsum composition so that the first liner is in an opposed relationship to the second liner and whereby the water resistant gypsum is positioned between the first and second liners; and

(iii) drying said layered product so as to allow hydration of the gypsum.

Figure 1

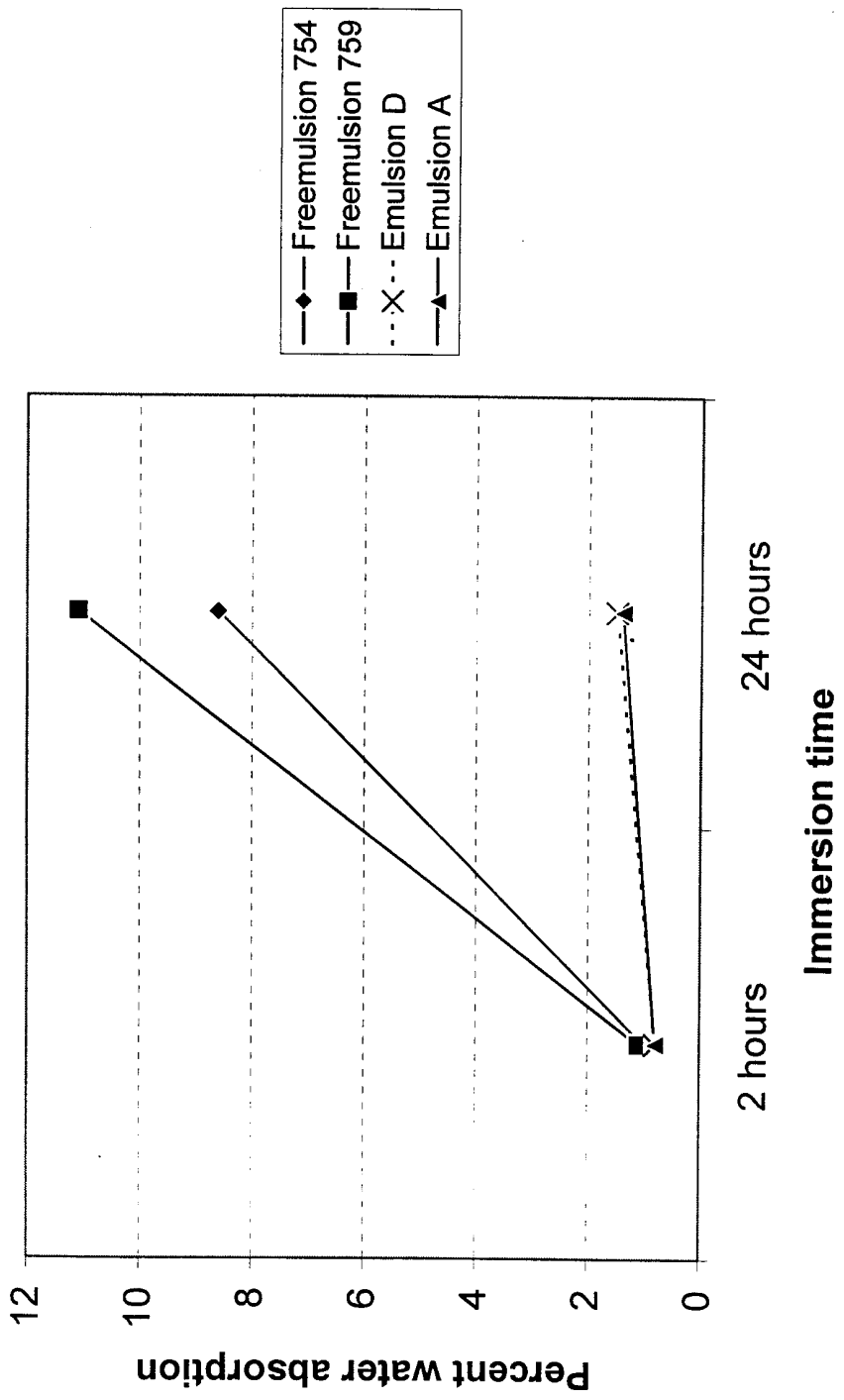

Freemulsion 754
Freemulsion 759
Emulsion D
Emulsion A
Percent water absorption
0
2
4
6
8
10
12
2 hours
24 hours
Immersion time

Figure 2

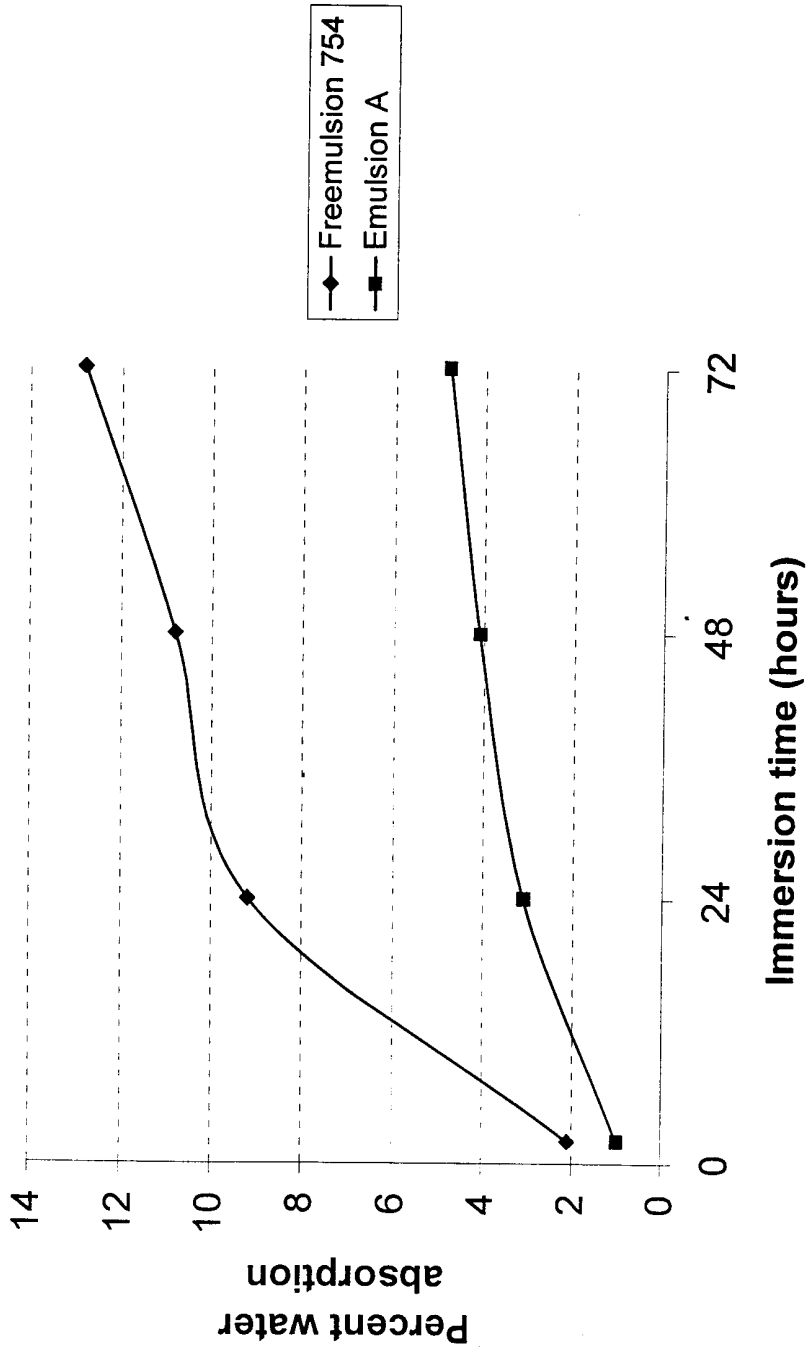
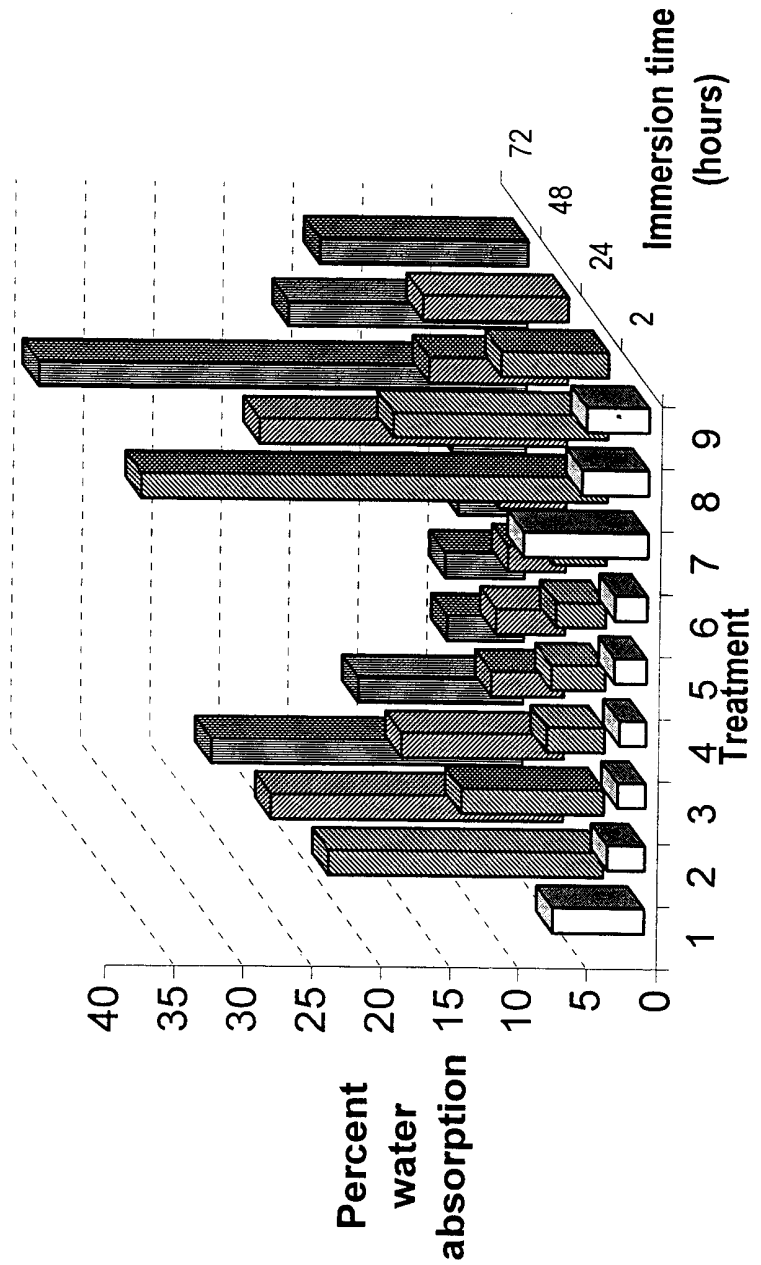

Freemulsion 754
Emulsion A
Percent water absorption
0
2
4
6
8
10
12
14
0
24
48
72
Immersion time (hours)

Figure 3


Percent water absorption
0
5
10
15
20
25
30
35
40
Treatment
1 2 3 4 5 6 7 8 9
Immersion time (hours)
2
24
48
72

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00331

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: C08L 91/06, 25/08, 25/12, 25/14, 25/16, 91/08; C04B 11/05, 11/06; B32B 13/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08L 91/06, 25/08, 25/12, 25/14, 25/16, 91/08; C04B 11/05, 11/06; B32B 13/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC AS ABOVE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT: WPAT, JPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession Number 93-357310, Class A97, JP 5-262956 A (KINDAI KAGAKU KK) 12 October 1993 abstract	1-3,6-7,11,15-17,19
X	Derwent Abstract Accession Number 99-029305, Class A92, JP 10-292290 A (SAIDEN KAGAKU KK) 4 November 1998 abstract	1-3,6-9,11,15-17,19
X	Derwent Abstract Accession Number 93-298032, Class A82, JP 5-209396 A (OSAKA PRINTING INK CO LTD) 20 August 1993 abstract	1-3,6-9,11,15-17,19

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 May 2000	13 JUN 2000

Name and mailing address of the ISA/AU	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00331

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 694597 A (DUSSEK CAMPBELL LIMITED) 31 January 1996 Example 1; page 6, lines 8-21; claims	1-3,6-9,15,19
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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END OF ANNEX