

WATER-DILUTABLE
PAINT

This invention relates to a water-dilutable paint and to certain preferred water-dilutable aqueous compositions and certain preferred addition polymers for use in the paint.

5 It is well known to employ a polymer containing carboxyl groups as a film-forming component of water-dilutable aqueous paints. Generally, these carboxyl groups are at least partially neutralised by a base such as an amine and
10 the composition normally comprises also a proportion of an organic cosolvent, usually of higher boiling point than water, in order to improve the solubility and rheological characteristics of the polymer in the aqueous phase.

15 Water-dilutable paints are preferred to paints based wholly on organic solvents such as white spirit for reasons of reduced cost, reduced toxicity and increased safety; and paints which yield coatings having a high level of gloss may be based on
20 this type of composition. However whilst a solution of film-forming polymer in an organic solvent, such as of an alkyd resin in white spirit, exhibits a uniform solids content/viscosity relationship when diluted with the same solvent, an aqueous solution of
25 a polymer containing carboxyl groups, for example an

addition co-polymer or a polyester such as are available commercially for use in coating compositions, does not show a uniform relationship when diluted with water. When a solution in a water-miscible cosolvent (e.g. a glycol ether) of a carboxyl group-containing polymer is progressively diluted with water from an initial polymer concentration of about 70% by weight in the co-solvent to a final polymer concentration of about 20% by weight in the diluted co-solvent, it is observed that the viscosity of the diluted solution passes through a minimum and then through a maximum before a uniform relationship between the solids content and the viscosity of the solution is resumed.

This anomalous behaviour on dilution with water of solutions of carboxyl-containing polymers in organic co-solvent, has been discussed by Overton & Herb in Journal of Coatings Technology, 55 (No. 700) May 1983, at page 33. It is a significant problem in the formulation of aqueous paints which contain carboxyl group-containing polymers since it can occur over the wide range of solids concentration at which these paints are used. Moreover the anomalous behaviour occurs in that region of polymer solids content which is most preferred for satisfactory application of paint to a substrate with a brush or by spray. When a paint is applied to a substrate and the aqueous phase gradually evaporates, assuming that the cosolvent present has a boiling point greater than that of water, the composition of the drying paint (and hence its rheology) follows in reverse the course which is followed when a solution of the polymer in the cosolvent is diluted with water. Thus there is reached a stage at which there is a rapid viscosity rise leading to stickiness

of application, followed by a temporary fall in the viscosity of the applied composition which causes paint applied to a vertical substrate to sag and to yield a final dry film of uneven thickness.

5 The problem can be avoided by formulating a paint at a very low solids content, but very thin coating films are then obtained and the application properties of this composition are unsatisfactory. The problem can be alleviated to some extent by
10 increasing the number of carboxyl groups and the extent to which they are neutralised by a base. However, this must always be a compromise since an increase in the number of carboxyl groups and the degree of neutralisation increases the
15 water-sensitivity of the final coating, and also the viscosity of the coating composition may be too high at a preferred polymer solids content. The problem is usually alleviated by the use of a cosolvent which is miscible with, and is of higher boiling point
20 than, water and normally a compromise has to be achieved between the acid value of the polymer, the degree of neutralisation and the proportion of cosolvent.

25 We have now found that improved paints can be based on aqueous solutions of certain selected water-dispersible polymers comprising both ionisable groups and non-ionisable water-soluble moieties. These solutions do not exhibit the anomalous increase in viscosity shown by solutions based on the polymers
30 previously used when diluted with water, and due to the presence of both ionisable groups and non-ionisable moieties, these solutions require only a minimum amount of an organic coupling solvent. At
35 most there will be used 150 parts by weight of the solvent per 100 parts by weight of polymer, if any at all. We have found that paints of this type can be

formulated for application to a substrate by brush which have improved application properties such as "brushability", "lapping" with composition which has been previously applied and flow-out of brush marks.

5 According to this invention we provide a water-dilutable paint which comprises a pigment and an aqueous coating composition which comprises:

A X parts by weight of water-dispersible film-forming polymer comprising

- 10 a) either anionisable groups, at least partially neutralised with a base when required, selected from -COOH , $\text{-SO}_3\text{H}$ and $\text{-PO}_4\text{H}_2$,
or cationisable groups, at least
15 partially neutralised with an acid when required, of structure $\text{-N R}^1\text{R}^2$, where R^1 and R^2 are H or C_{1-18} alkyl or substituted alkyl groups, the same or different, or R^1 and R^2
20 represent part of a cyclic structure and
b) non-ionisable water-soluble moieties selected from moieties of polyethylene glycol or its monoethers, moieties of
25 poly(meth)acrylamide, moieties of polyvinyl pyrrolidone and moieties of poly(2-ethyl oxazoline) or its hydrolysates

B Y parts by weight of an organic coupling solvent for the film-forming polymer which has a boiling
30 point greater than that of water and

C water

wherein the weight average molecular weight of the film-forming polymer is in the range 2000 to 15000, Y is from 0 to 1.5X, the molecular weight of moieties
35 of polyethylene glycol or its monoethers is not greater than 1000 and the molecular weight of

moieties of poly(meth)-acrylamide, of moieties of polyvinyl pyrrolidone or of poly(2-ethyl oxazoline) and its hydrolysates is not greater than 2000 whereby when a solution of X parts by weight of the water-dispersible polymer in Y parts by weight of the organic coupling solvent or, when Y = 0, in water is progressively diluted with water, there is no increase in viscosity of the diluted aqueous solution as measured at 25°C by a low shear viscometer.

This invention also provides a preferred water-dilutable aqueous coating composition which comprises:

A X parts by weight of water-dispersible film-forming polymer comprising

- a) either anionisable groups, at least partially neutralised with a base when required, selected from -COOH , -SO_3 and $\text{-PO}_4\text{H}_2$, or cationisable groups, at least partially neutralised with an acid when required, of structure $\text{-N R}^1\text{R}^2$, where R^1 and R^2 are H or C_{1-18} alkyl or substituted alkyl groups, the same or different, or R^1 and R^2 represent part of a cyclic structure and
- b) non-ionisable water-soluble moieties selected from moieties of polyethylene glycol or its monoethers, moieties of poly(meth)acrylamide, moieties of polyvinyl pyrrolidone and moieties of poly(2-ethyl oxazoline) or its hydrolysates

B Y parts by weight of an organic coupling solvent for the film-forming polymer which has a boiling point greater than that of water and

C water

wherein the weight average molecular weight of the film-forming polymer is in the range 2000 to 15000, Y is from 0.05X to 1.5X, the molecular weight of moieties of polyethylene glycol or its monoethers is not greater than 1000 and the molecular weight of poly(meth)-acrylamide, of moieties of polyvinyl pyrrolidone or of poly(2-ethyl oxazoline) and its hydrolysates is not greater than 2000 whereby when a solution of X parts by weight of the water-dispersible polymer in Y parts by weight of the organic coupling solvent is progressively diluted with water, there is no increase in viscosity of the diluted aqueous solution as measured at 25° by a low shear viscometer.

The invention further provides a preferred water-dispersible film-forming addition polymer which comprises polymerised vinyl and/or acrylic (including methacrylic) monomer and which is suitable for use in the above aqueous coating composition comprising:

a) either anionisable groups selected from $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{PO}_4\text{H}_2$, or cationisable groups of the structure $-\text{NR}^1\text{R}^2$ where R^1 and R^2 are H or C_{1-18} alkyl or substituted alkyl groups, the same or different, or R^1 and R^2 represent part of a cyclic structure,

and

b) non-ionisable water-soluble moieties selected from moieties of polyethylene glycol or its monoethers, moieties of poly(meth)acrylamide, moieties of polyvinyl pyrrolidone or moieties of poly(2-ethyl oxazoline) or its hydrolysates

wherein the weight average molecular weight of the film-forming addition polymer is in the range 2000 to 15000 and the molecular weight of moieties of

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polyethylene glycol or its monoethers, is not greater than 1000 and the molecular weight of moieties of poly(meth)acrylamide, moieties of polyvinyl pyrrolidone or of poly(2-ethyl oxazoline) and its hydrolysates is not greater than 2000.

By the term "organic coupling solvent" we mean any organic liquid, or mixture of liquids (including a blend of water-immiscible liquid and water-miscible liquid), present in the paint which forms a homogeneous mixture with the water dispersible polymer and water and which has a boiling point greater than water, i.e. greater than 100°C. The liquid should be inert towards the other ingredients of the paint.

Other inert organic liquids of boiling point 100°C or less which may also be present in the composition are to be disregarded in the characterising dilution/viscosity test mentioned above, and the test should be performed in their absence.

Suitable organic coupling solvents of boiling point greater than 100°C include alcohols, glycols, ester alcohols, ether alcohols and the esters of ether alcohols for example : n-butanol, 2-pentanol, ethylene glycol, benzyl alcohol, 2,2,4 trimethylpentane 1,3 diol-monoisobutyrate, ethylene glycol monomethyl, -ethyl, -propyl, -butyl and -hexyl ethers, propylene glycol mono-methyl, -ethyl, -propyl and -butyl ethers, diethylene glycol, dipropylene glycol, dispropylene glycol methyl ether, diethylene glycol ethyl ether, ethylene glycol monomethyl ether acetate and propylene glycol monomethyl ether acetate.

It is preferred to use propylene glycol ethers and their ester derivatives because they are of low odour, good solvency and low toxicity.

Whilst paints according to the invention may be free from organic coupling solvent, in general we find that in preferred coating compositions a certain proportion of solvent is usually necessary but that the selection of film-forming polymers comprising both ionisable and non-ionisable water-soluble groups which avoid an increase in viscosity on dilution keep this proportion to a minimum. In general there may be present in the composition at least 5 parts by weight of organic coupling solvent/100 parts by weight of polymer but there will be present not more than 150 parts by weight of this solvent/100 parts by weight of polymer, that is to say Y shall not exceed 1.5X and is preferably from 0.05X to 1.5X.

The water-dispersible film-forming polymer may be selected from a wide range of chemical types, for example vinyl or acrylic addition polymers, polyesters, polyurethanes, polyureas, polyamides, polyethers or epoxides.

Preferably the water-dispersible film-forming polymer is of a type which permits the regular distribution of the ionisable and non-ionisable water-soluble groups along its length.

Preferred types of film-forming polymer, for this reason, are vinyl or acrylic addition polymers, polyesters, polyurethanes and polyureas, which are prepared by procedures enabling good control of molecular weight.

Suitable bases which can be used to at least partially neutralise anionisable groups, when these groups are present and when neutralisation is required, are inorganic bases such as sodium hydroxide, potassium hydroxide and ammonia; and organic bases such as amines, for instance dimethyl aminoethanol, triethylamine, dibutylamine or

morpholine.

Suitable acids which can be used to at least partially neutralise cationisable groups, when these groups are present and when neutralisation is required, are inorganic acids such as hydrochloric, phosphoric, boric, sulphuric and sulphonic acids; and organic acids such as acetic, lactic, formic and glycollic acids.

Different levels of water-soluble groups are preferred for different polymer types, depending on the hydrophilicity or hydrophobicity of the backbone polymer and the solubility of the water-soluble groups selected. However in general, the level of ionisable groups is in the range 0.3 to 3.6 moles/kg of polymer and the non-ionisable water-soluble moieties are present in a total proportion of 0.5 to 53.8% by weight of the polymer.

We have found that there is an optimum distribution of the total weight of non-ionisable water-soluble material present and the number of distinct moieties present in a polymer which comprise such material. For example, in the polyester of Example 1 there is present a total of 54% by weight based on the film-forming polymer of moieties of methoxypolyethylene glycol, and only when this is contained in individual non-ionisable groups of molecular weight about 600 or less, does the polymer solution satisfy the dilution/viscosity test and is therefore within the scope of this invention.

It is a general principle that the non-ionisable water-soluble moieties should be evenly distributed throughout the polymer, i.e. the ratio of the number of soluble groups to the total weight of non-ionisable water-soluble material should be high. More specifically, the quantity and molecular

weight of the non-ionisable water-soluble moieties should be such that, on average, there is more than one water-soluble moiety of this type per polymer molecule.

5 In the formulation of water-dilutable
paints according to this invention, one important
characteristic of a suitable water-dispersible
polymer is that it quickly becomes insensitive to
water after application to a substrate. This may be
10 achieved by minimising the proportions of ionisable
groups (and the degree of neutralisation) and
non-ionisable water-soluble moieties, and balancing
this by an increasing proportion of organic coupling
solvent; and/or by the incorporation of crosslinkable
15 groups, e.g. autoxidisable groups, or crosslinking
agents which subsequently produce a complex
structure.

A preferred polymer containing anionisable
groups for use in such paints is an acrylic addition
20 copolymer of molecular weight in the range 6000 to
12000 which comprises carboxyl groups and moieties of
a polyethylene glycol (introduced, for example, by
using methoxypolyethylene glycol (meth)acrylate as a
comonomer) of molecular weight in the range 200 to
25 550, the total weight of the non-ionisable material
not exceeding 20% and preferably not exceeding 10% by
weight based on the weight of the film-forming
polymer, and the acid value in the range 20 to 200 mg
KOH/g, preferably 50 to 120 mg KOH/g.

30 Another preferred polymer containing
anionisable groups is an acrylic addition copolymer
containing carboxyl groups as above, and comprising
moieties of poly(meth)acrylamide at a level not
exceeding 20% and preferably not exceeding 10% by
35 weight of the polymer.

Typical acid comonomers for use in

preparing a suitable film-forming addition polymer, in conjunction with for example a poly(meth)-acrylamide-containing derivative of (meth)acrylic acid or methoxypolyethylene glycol (meth)acrylate, include (meth)acrylic acid, itaconic acid, citraconic acid, crotonic acid, sorbic acid and fumaric acid. Typical additional comonomers include for instance methyl methacrylate, butyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, lauryl methacrylate, styrene and methyl styrene, vinyl acetate, vinyl chloride, vinylidene chloride, acrylonitrile and allyl alcohol. Particularly suitable polymers are those comprising (meth)acrylic acid, with methyl methacrylate, butyl acrylate and/or 2-ethylhexyl acrylate.

A preferred polymer containing cationisable groups is an acrylic copolymer of molecular weight in the range 6000 to 12000 which comprises amine groups and moieties of polyethylene glycol, for instance methoxy polyethylene glycol of molecular weight in the range 200 to 550 (350), and/or moieties of poly(meth)acrylamide, the total weight of the nonionic water-soluble material not exceeding 20% by weight of the polymer (10%) and the amine value 20 to 200 mg KOH/g, preferably 50 to 120 mg KOH/g.

Typical basic comonomers for use in preparing a suitable polymer include dimethylamino-ethyl methacrylate, 2-vinyl pyridine, 4-vinyl pyridine, 3-dimethylamino acrylonitrile. Typical additional comonomers include for instance methyl methacrylate, butyl acrylate, ethyl acrylate, ethylhexyl acrylate, lauryl methacrylate, styrene, 2-methyl styrene, vinyl acetate, vinyl chloride, vinylidene chloride, acrylonitrile and allyl alcohol.

The non-ionisable water-soluble moieties of poly(meth)acrylamide, polyvinyl pyrrolidone and poly 2-ethyl oxazoline which are specified as useful in

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this invention are not discussed or exemplified in the same detail as moieties of polyethylene glycol but bearing in mind their similar properties, it is believed that their behaviour will be broadly similar to that of the polyethylene glycol moieties.

5 The preferred aqueous coating compositions of this invention may be used in a wide variety of applications. Although they are of primary value in the formulation of water-dilutable paints they may also find use in the formulation of adhesives, horticultural compositions, pharmaceutical compositions etc.

10 The paints may comprise other materials such as other polymers and additives, for example fillers, crosslinking agents, anti-skinning agents, slip aids etc.

15 The invention is illustrated by the following Examples in which parts and percentages are by weight.

EXAMPLE 1

20 This Example describes the preparation of a series of four polyesters, each of molecular weight (weight average) in the range 4000 to 6000, which contain carboxyl groups and water-soluble moieties of methoxy polyethylene glycol of molecular weight varying in the range 350 to 2000. The graphs in the accompanying drawing illustrate the importance of the molecular weight of each water-soluble moiety, for a given total weight of such moieties present, in determining the rheology of an aqueous solution of the polyester.

25 30 With reference to Table 1 below, four polyesters, References 1, 2, A and B (the letters

denote comparative polymers), were prepared by reacting a) parts of adipic acid, b) parts of dimethylolpropionic acid, c) parts of neopentyl glycol and d) parts of a methoxy polyethylene glycol (approximately the same weights in each case but see Table 1 for the different molecular weight in each case) in a reaction flask fitted with a stirrer, thermometer, steam condenser and a Dean & Stark trap and connected to a nitrogen supply. 0.3% of isopropyl titanate and 3% of toluene (each by weight based on the total weight of reactants) were added and the mixture refluxed at 190°C until reaction was substantially complete.

TABLE 1

Molecular weight of methoxypoly-ethylene glycol	350	550	750	2000
Reactants ref.				
a	657.0	657.0	657.0	657.0
b	469.0	301.5	227.8	107.2
c	52.0	182.0	239.2	332.8
d	1137.5	1100.0	1087.5	1140.0
Polyester reference no.	1	2	A	B

The resulting polyesters each had a molecular weight (weight average) in the range 4000 to 6000 and an acid value in the range 25 to 45 mg KOH/g. Each was dispersed in the absence of base in

distilled water to give a range of sample solutions of solids content (by weight) in the range 20 to 95%. The viscosity of each sample was measured at 25°C with a Brookfield low-shear viscometer and this viscosity was plotted against the corresponding solids content as shown in the accompanying drawing.

It will be noted that only solutions of polyesters References 1 and 2 show no increase in viscosity on dilution with water and therefore only these solutions are useful in paints according to the invention. This was achieved in the absence of organic coupling solvent and of neutralising base.

EXAMPLE 2

a) This Example describes the preparation of three polyesters of molecular weight (weight average) in the range 4000 to 6000 by the procedure of Example 1 but the methoxypoly- ethylene glycol was of molecular weight 550 in each case and the proportions used were varied.

The polyesters were prepared as described, and using the same components a, b, c and d as in Example 1. The proportions of the components are given in Table 2.

TABLE 2

Reactants	% weight of moiety of methoxypoly-ethylene glycol mol wt 550	(based on total weight of polymer)		
	ref.	53.4%	46.4%	36.7%
a		657.0	657.0	657.0
b		301.5	234.5	167.5
c		182.0	234.5	286.0
d		1100.0	825.0	550.0
Polyester reference no.		3	C	D

The resulting polyesters all had a molecular weight (weight average) in the range 4000 to 6000 and an acid value in the range 35 to 60 mg KOH/g. Each was dispersed in the absence of base in distilled water to give a range of sample solutions of solids content (by weight) in the range 20 to 95%. The viscosity of each sample was measured at 25°C with a Brookfield viscometer and this viscosity was plotted against the corresponding solids content, as illustrated for Example 1.

It was found that only solutions of polyester Reference 3 showed no increase in viscosity on dilution with water. Therefore only this solution is useful in a paint according to the invention.

This was achieved in the absence of coupling solvent and of neutralising base.

b) Four further polyesters, References E, F, 4 and 5, in which the proportions of methoxypoly-ethylene glycol were respectively 29.8%, 35.5%, 45.0%

and 53.8% by weight, were prepared by the procedure of Example 1, but using methoxy polyethylene glycol of molecular weight 350. It was found from a plot of viscosity/solids content that only the solutions of polyesters 4 and 5 are useful in a paint according to the invention. This was achieved in the absence of organic coupling solvent and of neutralising base.

EXAMPLE 3

This Example describes the preparation of a series of polyesters by a two-stage process in which only components a), b) and c) of the polyester described in Example 1 were co-reacted in a first stage and in a second stage the resulting polyester was post-esterified with different amounts of an allyloxypolyethylene glycol in which the polyethylene glycol moiety had a molecular weight of 300, 0.1% of Fascat 4101 (commercially available from M & T Chemicals) was used as catalyst instead of the isopropyl titanate of Example 1. The proportions a), b) and c) of the components of the first stage polyester are given in Table 3. They were co-reacted until an acid value x) mg KOH/g was reached. d) parts of the allyloxypolyethylene glycol were added to the product of the first stage and the mixture refluxed at 210° to 220°C until reaction was complete.

The resulting polyesters each had a molecular weight (weight average) in the range 6000 to 7000 and an acid value in the range 50 to 80 mg KOH/g. They were neutralised with di-methylaminoethanol to 105% of the final acid value. They were each diluted with distilled water to give a range of sample solutions varying in solids content from 20% to 90% and their viscosities measured using a

Brookfield lowshear viscometer. It was found from a plot of viscosity against solids content, as described in Example 1, that only the solutions of polyesters Reference Nos. 6, 7, 8 and 9 were useful in a paint according to the invention. This was achieved in the absence of a coupling solvent.

TABLE 3

allyloxy- polyethyl- ene glycol	40.3	33.1	26.0	17.0	10.0
Reactants mol. wt ref. % 350					
a	657.0	657.0	657.0	657.0	657.0
b	281.4	214.4	160.8	107.7	73.7
c	197.6	249.6	291.2	332.8	358.8
x	175	149	128	102	92
d	647.5	472.5	332.5	192.5	105.0
Polyester reference no.	6	7	8	9	G

EXAMPLE 4

This Example describes the preparation of a series of acrylic copolymers containing carboxyl groups and an increasing proportion of moieties of methoxypolyethylene glycol of molecular weight 350.

20 parts of propylene glycol monomethyl ether were charged to a reaction flask fitted with stirrer, thermometer, and reflux condenser and heated to reflux. With reference to Table 4 below, 5 parts of azodiiso-butyronitrile were added to a mixture of

x) parts of a 6:4 mixture of methyl methacrylate and butyl acrylate, y) parts of methacrylic acid and z) parts of methoxypolyethylene glycol methacrylate (in which the methoxypolyethylene glycol moiety was of a molecular weight 350). The mixture was stirred at room temperature until clear and then pumped into the reaction flask over a period of 3 hours. 30 minutes after the end of the feed 1, part of azodiisobutyronitrile was added and reflux maintained for a further 60 minutes, after which the resin was cooled and solids adjusted to 70% with additional propylene glycol monomethyl ether. The acid value of the resin was 65 mg KOH/g and the resin was neutralised with di-methylaminoethanol and, as in Example 3, distilled water was added to give a range of solutions varying in solids content from 20% to 70%. The viscosities of these solutions were measured using a Brookfield low-shear viscometer. It was found from a plot of viscosity against solids content, as described in Example 1, that only solutions of acrylic copolymers References 10 and 11 were useful in a paint composition according to the invention when using the specified proportion of coupling solvent and neutralising base.

TABLE 4

Reactants ref.	% methoxypoly- ethylene glycol				
	0	10	20	30	40
meth- acrylate					
x	90	80	70	60	50
y	10	10	10	10	10
z	0	10	20	30	40
Acrylic copolymer	H	I	J	10	11

EXAMPLE 5

This Example describes the preparation of a polyurethane of molecular weight (weight average) approximately 15000 containing carboxyl groups and moieties of methoxypolyethylene glycol of molecular weight 350; and the preparation of aqueous solutions in the presence of water-miscible and water-immiscible organic solvents.

428.8 parts of Desmodur N (a tolylene diisocyanate commercially available from Bayer:

"Desmodur" is a Registered Trade Mark), 0.1 parts dibutyl tin dilaurate and 200 parts methylethyl ketone was charged to a reaction flask fitted with stirrer, thermometer and reflux condenser. 154 parts of methoxypolyethylene glycol (molecular weight 350) were added over a period of 30 minutes at 60°C under a blanket of nitrogen gas. After heating at 60°C for 60 minutes, 59.5 parts of ethylene glycol monoethyl ether were added to the mixture over a period of 15

minutes. After a further 60 minutes at 60°C, 73.3 parts of polypropylene glycol (molecular weight 400) were added over a period of 15 minutes. After a final period of 60 minutes at 60°C, the mixture was cooled to 10°C and a mixture of 55 parts of glycine, 65.3 parts of dimethyl amino ethanol, 500 parts of distilled water and 150 parts of isopropyl alcohol was added rapidly with stirring. When reaction was complete, the mixture was vacuum stripped to remove all solvents, and solutions prepared at 75% solids in the following solvents (1, 2 and 3 are organic coupling solvents according to the invention):

- 1) propylene glycol monomethylether
- 2) benzyl alcohol
- 3) the acetate of ethylene glycol monomethyl ether
- 4) distilled water

As in Example 4, distilled water was added to these solutions to give a range of aqueous solutions varying in solids content from 20% to 70%. The viscosities of these solutions were measured using a Brookfield low-shear viscometer. It was found that all four polymer solutions were useful in paints according to the invention when a plot of viscosity against solids content was prepared.

EXAMPLE 6

This Example describes the preparation of two addition polymers each containing basic groups and different proportions of moieties of methoxypolyethylene glycol (molecular weight 350).

The two polymers, (a) and (b), were prepared by the procedure described in Example 4, the

monomer compositions (parts) being as follows:

	(a)	(b)
Methyl methacrylate	54.5	43.0
Methoxy polyethylene glycol acrylate	10.0	30.0
Butyl acrylate	25.5	17.0
methacrylate	10.0	10.0
	100	100

The polymers were obtained as a 50% solids solution in propylene glycol monomethylether and were shown by gas phase chromatography to be of similar molecular weights in the range 5500 to 6000. Glacial acetic acid was added to bring the pH to 7 and appropriate amounts of water were added to provide a range of sample solutions from 20% to 50% solids content. It was found from a plot of viscosity against solids content, as described in Example 1, that only the aqueous solution of polymer (b) was useful in a paint according to the invention in the presence of organic coupling solvent and neutralising acid.

EXAMPLE 7

Addition polymers similar to those described in Example 4, were prepared but in which the carboxyl groups were replaced by either a molar equivalent of sulphonate groups or of phosphate groups. They were neutralised with ammonia, diluted with water and a plot made of viscosities corresponding to various solids contents, as

described in Example 1. The solutions of polymers containing 20, 30 and 40% of methoxypolyethylene glycol moieties were in accordance with the invention when using the amounts of organic coupling solvent specified in Example 4.

EXAMPLE 8

This Example describes the preparation of a paint according to the invention.

An aqueous gloss paint (A) was prepared by dispersing in a ball mill 61.5 parts of rutile titanium dioxide, 25 parts of a 75% solids solution in water of the polyester prepared in Example 1, Reference No. 1, and 20 parts of water. A further 88.3 parts of the polyester solution at 75% solids were added to the millbase with stirring and the resulting paint thinned to 4 poise measured at 25°C and at 10000 secs⁻¹. A similar paint (B) was based on the polyester of Example 1, Reference A.

Both paints were applied to a vertical surface by brush. Paint (A) was easy to apply and the wet edge of the paint film could be taken up after 10 minutes. The paint film showed no evidence of sagging from the thick edge. Paint (B) was more difficult to apply in that it became sticky more quickly and the wet edge of the paint film was less readily taken up than that of (A). Considerable sagging of the film occurred on loss of water due to the decrease in viscosity which occurred when the solids content increased, as is illustrated in the attached drawing with reference to Example 1.

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EXAMPLE 9

5 When the moieties of polyethylene glycol or the monoether used in the previous Examples were replaced by moieties of poly(meth)acrylamide, polyvinyl pyrrolidone or poly 2-ethyl oxazoline all of molecular weight less than 2000, generally similar results were obtained with these moieties when they were of similar molecular weight to those moieties used in Examples which provided polymer solutions for use in the paints of this invention.

CLAIMS:

1. A water-dilutable paint which comprises a pigment and an aqueous coating composition which comprises:

A X parts by weight of water-dispersible film-forming polymer comprising

a) either anionisable groups, at least partially neutralised with a base when required, selected from -COOH , $\text{-SO}_3\text{H}$ and $\text{-PO}_4\text{H}_2$,
or cationisable groups, at least partially neutralised with an acid when required, of structure $\text{-N R}^1\text{R}^2$, where R^1 and R^2 are H or C_{1-18} alkyl or substituted alkyl groups, the same or different, or R^1 and R^2 represent part of a cyclic structure and

b) non-ionisable water-soluble moieties selected from moieties of polyethylene glycol or its monoethers, moieties of poly(meth)acrylamide, moieties of polyvinyl pyrrolidone and moieties of poly(2-ethyl oxazoline) or its hydrolysates,

B Y parts by weight of an organic coupling solvent for the film-forming polymer which has a boiling point greater than that of water and

C water

wherein the weight average molecular weight of the film-forming polymer is in the range 2000 to 15000, Y is from 0 to 1.5X, the molecular weight of moieties of polyethylene glycol or its monoethers is not greater than 1000 and the molecular weight of moieties of poly(meth)-acrylamide, of moieties of polyvinyl pyrrolidone or of poly(2-ethyl oxazoline) and its hydrolysates is not greater than 2000 whereby



when a solution of X parts by weight of the water-dispersible polymer in Y parts by weight of the organic coupling solvent or, when $Y = 0$, in water is progressively diluted with water, there is no increase in viscosity of the diluted aqueous solution as measured at 25°C by a low shear viscometer.

2. A paint according to Claim 1 wherein Y is from 0.05X to 1.5X.
3. A paint according to Claim 1 or Claim 2 wherein the organic coupling solvent is selected from alcohols, glycols, ester alcohols, ether alcohols and esters of ether alcohols.
4. A paint according to Claim 3 wherein the organic coupling solvent is a propylene glycol ether or an ester derivative thereof.
5. A paint according to any one of Claims 1 to 4 wherein ionisable groups and non-ionisable water-soluble moieties are regularly distributed along the length of the film-forming polymer.
6. A paint according to any one of Claims 1 to 5 wherein there is more than one non-ionisable water-soluble moiety per molecule of polymer.
7. A paint according to any one of Claims 1 to 6 wherein the molecular weight of moieties of polyethylene glycol or its monoethers is not more than 600.
8. A paint according to any one of Claims 1 to 7 wherein the film-forming polymer comprises from 0.5 to 53.8 wt % (based on the total weight of the polymer) of non-ionisable water-soluble moieties.
9. A water-dilutable aqueous coating composition which comprises:
A X parts by weight of water-dispersible film-forming polymer comprising



5 a) either anionisable groups, at least
partially neutralised with a base
when required, selected from $-\text{COOH}$,
 $-\text{SO}_3\text{H}$ and $-\text{PO}_4\text{H}_2$,
or
10 cationisable groups, at least
partially neutralised with an acid
when required, of structure $-\text{N R}^1\text{R}^2$,
where R^1 and R^2 are H or C_{1-18} alkyl
or substituted alkyl groups, the
15 same or different, or R^1 and R^2
represent part of a cyclic structure
and

15 b) non-ionisable water-soluble moieties
selected from moieties of polyethylene
glycol or its monoethers, moieties of
poly(meth)acrylamide, moieties of polyvinyl
pyrrolidone and moieties of poly(2-ethyl
oxazoline) or its hydrolysates,

20 B Y parts by weight of an organic coupling solvent
for the film-forming polymer which has a boiling
point greater than that of water and

C water
wherein the weight average molecular weight of the
film-forming polymer is in the range 2000 to 15000, Y
25 is from 0.05X to 1.5X, the molecular weight of
moieties of polyethylene glycol or its monoethers is
not greater than 1000 and the molecular weight of
moieties of poly(meth)-acrylamide, of moieties of
polyvinyl pyrrolidone or of poly(2-ethyl oxazoline)
30 and its hydrolysates is not greater than 2000 whereby
when a solution of X parts by weight of the
water-dispersible polymer in Y parts by weight of the
organic coupling solvent ~~or, when Y = 0, in water~~ is
progressively diluted with water, there is no
35 increase in viscosity of the diluted aqueous solution
as measured at 25°C by a low shear viscometer.



10. An aqueous coating composition according to Claim 9 wherein the organic coupling solvent is selected from alcohols, glycols, ester alcohols, ether alcohols and esters of ether alcohols.
- 5 11. An aqueous coating composition according to Claim 10 wherein the organic coupling solvent is a propylene glycol ether or an ester derivative thereof.
- 10 12. An aqueous coating composition according to any one of Claims 9 to 11 wherein ionisable groups and non- ionisable water-soluble moieties are regularly distributed along the length of the film-forming polymer.
- 15 13. An aqueous coating composition according to any one of Claims 9 to 12 wherein there is more than one non-ionisable water-soluble moiety per molecule of polymer.
- 20 14. An aqueous coating composition according to any one of Claims 9 to 13 wherein the molecular weight of moieties of polyethylene glycol or its monoethers is not more than 600.
- 25 15. An aqueous coating composition according to any one of Claims 9 to 14 wherein the film-forming polymer comprises from 0.5 to 53.8 wt % (based on the total weight of the polymer) of non-ionisable water-soluble moieties.
- 30 16. A water-dispersible film-forming addition polymer which comprises polymerised vinyl and/or acrylic (including methacrylic) monomer and which is suitable for use in a paint according to Claim 1 or in an aqueous coating composition according to Claim 9 wherein the polymer comprises
- a) either anionisable groups selected from $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{PO}_4\text{H}_2$, or cationisable groups of the structure



$-NR^1R^2$ where R^1 and R^2 and H or C_{1-18} alkyl or substituted alkyl groups the same or different, or R^1 and R^2 represent part of a cyclic structure,

5

and

10

15

- b) non-ionisable water-soluble moieties selected from moieties of polyethylene glycol or its monoethers, moieties of poly(meth)acrylamide, moieties of polyvinyl pyrrolidone or moieties of poly(2-ethyl oxazoline) or its hydrolysates and wherein the weight average molecular weight of the film-forming polymer is in the range 2000 to 15000 and the molecular weight of moieties of polyethylene glycol or its monoethers is not greater than 1000 and the molecular weight of moieties of poly(meth)acrylamide, moieties of polyvinyl pyrrolidone or of poly(2-ethyl oxazoline) and its hydrolysates is not greater than 2000.
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