

WATER-BASED AUTOXIDISABLE AIR-DRYING COATING COMPOSITION
AND COPOLYMERS FOR USE IN IT

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This invention relates to a water-based autoxidisable air-drying coating composition, especially a gloss (including partial gloss) coating composition suitable for application at ambient temperatures which comprises water, possible some organic cosolvent and a salt of partially esterified carboxylic acid film-forming copolymer. The invention also relates to a coating composition of this type which additionally comprises dispersed particles of water-insoluble organic polymeric material. The invention further relates to an optionally neutralised partially esterified carboxylic acid film-forming copolymer which is suitable for use in these coating composition when suitably neutralised.

The coating composition will generally be a paint, varnish or woodstain applicable by brush, roller, pad or spray to architectural surfaces, fittings or furnishings, that is to say surfaces usually found in buildings and furniture. A good paint or varnish for use on such surfaces must lap well at ambient temperatures, that is to say when adjacent and overlapping bands of paint are applied to a substrate one after another and allowed to dry, it should be difficult for a casual observer to detect a boundary between adjacent contiguous bands of dried paint even when one band was applied several minutes after the other. The best paints lap well even when the application of adjacent contiguous bands is separated by as much as 5 minutes. The same is true for varnishes.

Hitherto the lapping ability of water-based decorative paints has been inferior to that of organic solvent-based paints, especially solvent-based paints comprising alkyd resin and white spirit. This inferiority is particularly noticeable with gloss or partial gloss paints, that is to say paints which dry to produce a coating having a specular gloss at an angle of 60° of at least 30% (or at least 65% for high gloss) where specular gloss at 60° is measured according to ASTM Test D523 using light reflected at an angle of 60° to the normal to the surface of the paint. Water-based air-drying gloss paints have been proposed which comprise water and an aqueous colloidal dispersion of water-insoluble film-forming polymer (including copolymers) such as for example a polymer or co-polymer of alkyl acrylate (including

methacrylate). When such paints dry on a surface, the particles of polymer begin to coalesce to form a coherent film of coalesced particles which coats the surface but which dries so quickly that the particles of film-forming polymer begin to coalesce too quickly. This means that in practice there is not always time for a band of paint to lap with a subsequently applied adjacent contiguous band. Failure to lap creates unsightly evidence of joins in a coating composition of the type which dries to produce a gloss or partial gloss finish.

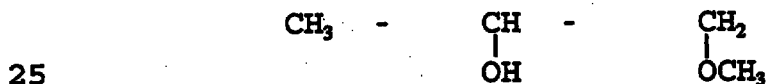
Attempts were made to improve lapping ability by slowing down the speed at which the water-based paint dried. This was done by adding high boiling solvent to the water. Some improvement was achieved, but the lapping ability was still unacceptably low, falling well short of what could be achieved from solvent-based paint. In addition the slowing down of drying is in itself undesirable because wet coatings ought to dry as quickly as possible. Usually a wet coating should become dry to the touch after 10 (preferably after 6) hours at ambient temperatures and dry enough to receive a further coating usually after 48 (preferably after 16) hours from application. It was further found that slow drying coatings were also vulnerable to unsightly disfiguration by water especially when the coating composition contained pigments.

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Preferably coating compositions should also have a good resistance to discolouration (more particularly yellowing) with age.

5 An object of this invention is to provide a water-based autoxidisable coating composition suitable for use at ambient temperatures which laps well yet dries quickly in air and achieves an adequate resistance to disfiguration by water. A refinement of the invention provides a coating
 10 composition having improved resistance to discolouration on ageing. Another refinement of the invention provides a coating composition having improved gloss. Another objective of the invention is to provide a carboxylic acid film-forming copolymer which is suitable for use in coating
 15 compositions of this invention when suitably neutralised.

It has now been discovered that solution viscosity as measured in 1-methoxy-2-hydroxy propane (MHP) by an oscillatory parallel plate rheometer can be used to select
 20 certain specified partially esterified carboxylic acid film-forming copolymers which enable the above objectives to be met. MHP is



Accordingly this invention provides a water-based autoxidisable air-drying coating composition suitable for
 30 application at ambient temperatures which comprises water, 0 to 50 wt% organic cosolvent (based on the weight of water and cosolvent) and a salt of monovalent cations and partially esterified carboxylic acid film-forming copolymer at least partially neutralised by the cations wherein

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a) the partially esterified carboxylic acid copolymer comprises

10 (i) copolymerised acid monomer/s derived by copolymerisation of at least one unsaturated carboxylic acid monomer or its anhydride and which copolymerised monomer/s provide carboxylic acid groups to the copolymer,

15 (ii) copolymerised non-acid monomer and

(iii) 15 to 38 wt% (based on the weight of the partially esterified carboxylic acid copolymer before neutralisation) of 3-allyloxy-2-hydroxypropyl moieties or their 2-methylallyl analogue (ie $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{CH}_2-\text{CR}=\text{CH}_2$ where R is H or CH_3) by which the carboxylic acid copolymer is partially esterified,

25 b) the acid value of the partially esterified carboxylic acid copolymer before neutralisation is from 25 to 60 mg KOH/g unneutralised partially esterified copolymer and

c) the nature of the partially esterified carboxylic acid copolymer is such that before neutralisation the copolymer 30 gives a solution viscosity of from 1 to 500 Pa.sec when measured at 60°C on a solution consisting of 90 wt% unneutralised partially esterified carboxylic acid copolymer and 10 wt% 1-methoxy-2-hydroxy propane (MHP) using an oscillatory parallel plate rheometer. This 35 invention also provides a partially esterified carboxylic acid film-forming copolymer wherein

5 a) the partially esterified carboxylic acid copolymer comprises

10 (i) copolymerised acid monomer/s derived by copolymerisation of at least one unsaturated carboxylic acid monomer or its anhydride and which copolymerised monomer/s provide carboxylic acid groups to the copolymer

(ii) copolymerised non-acid monomer and

15 (iii) 15 to 38 wt% of 3-allyloxy-2-hydroxypropyl moieties or their 2-methylallyl analogue by which the carboxylic acid copolymer is partially esterified

20 b) the acid value of the partially esterified carboxylic acid copolymer (prior to any neutralisation which may be subsequently performed) is from 25 to 60 mg KOH/g partially esterified copolymer and

25 c) the nature of the partially esterified carboxylic acid copolymer is such that the copolymer gives a solution viscosity of from 1 to 500 Pa.sec when measured at 60°C on a solution consisting of 90 wt% unneutralised partially esterified carboxylic acid copolymer and 10 wt% 1-methoxy-
30 2-hydroxy propane (MHP) using an oscillatory parallel plate rheometer. When used in a coating according to this invention, the partially esterified carboxylic acid copolymer will have been converted to a salt by at least partial neutralisation by monovalent cations.

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Good lapping requires that the salt of the partially esterified carboxylic acid copolymer be dissolved in the liquid component of the coating composition as opposed to merely being present as a dispersion of solid particles. However, the salt generally does not form a perfect solution because its solutions are usually not fully transparent. Instead they scatter light to a small extent and may appear hazy when the coating composition contains little or no organic cosolvent. In practice, the nature of the partially esterified copolymer which provides the anionic moieties to the salt is generally such that where the copolymer is fully neutralised by sodium cations, the salt produced is soluble at least to the extent that a solution comprising 25 wt% anionic moieties of the salt and 75 wt% of a mixture of equal weights of water and 1-methoxy-2-hydroxy propane (MHP) (where the percentage is based on the combined weights of anionic moiety, water and MHP) appears clear to the unaided eye after the solution has stood for 48 hours at 20°C. Preferably the salt of the partially esterified carboxylic acid copolymer when fully neutralised should be soluble to the extent that the solution comprising 25 wt% anionic moieties of the salt and 75 wt% of a 4:1 (by weight) mixture of water and MHP after standing for 48 hours at 20°C has a nephelometer turbidity reading of less than 80 nephelometer turbidity units (NTU) as measured by the Clarity Assessment Technique hereinafter described. To obtain a high degree of dissolution, it is preferred that enough monovalent cation should be present to neutralise at least 75% (most preferably at least 90%) of the carboxylic acid groups which

remain. Usually the copolymer will be fully neutralised. An excess of cations may be present if an alkaline composition is required.

5 It is also important that the salt should form a stable solution. It has been found that if the acid value of the carboxylic acid copolymer before neutralisation falls below 25 mgKOH/g unneutralised copolymer, then the neutralised copolymer will slowly
10 precipitate over a period of several days. On the other hand, if the acid value exceeds 60, the coating compositions develop unacceptably poor water resistance.

15 Good lapping combined with short drying times requires the selection of partially esterified copolymers having a particular balance of macromolecular properties such as molecular weight, molecular weight distribution and no doubt other
20 macromolecular characteristics not yet appreciated. The nature of this balance is far from understood but it has been discovered that solution viscosities of unneutralised partially esterified copolymers in
25 1-methoxy-2-hydroxy propane (MHP) when measured using an oscillatory parallel plate rheometer reliably identify those partially esterified copolymers which are suitable. MHP may be obtained from Dow Chemical Company under the trade name "Dowanol" PM. "Dowanol"
30 PM may contain up to 1 wt% of 1-hydroxy-2-methoxy propane and up to 5 wt% of hygroscopically absorbed water as impurities. These impurities have no significant effects and they are assumed to be non-existent when calculating the amounts of MHP used. If this solution viscosity exceeds 500 Pa.sec,

The copolymer is conveniently partially esterified by adding allyl glycidyl ether which is



or its methallyl analogue to some of the carboxylic acid groups via a ring opening of the oxirane ring to provide partially esterified carboxylic acid copolymer as follows

$$\begin{array}{c} \text{--CH}_2 - \text{C} \text{---} \text{copolymer chain} \text{---} \text{CH}_2 - \text{C} \text{---} \\ | \qquad \qquad \qquad | \\ \text{O} = \text{C} - \text{O} - \text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH} = \text{CH}_2 \qquad \qquad \text{O} = \text{C} - \text{O} - \text{CH}_2 - \text{CH} = \text{CH}_2 \end{array}$$

Only some of the acid groups react with the allyl or methallyl glycidyl groups with the result that some acid groups remain available for neutralisation to form the salt. The 3-(meth)allyloxy-2-hydroxypropyl groups allow the copolymer to undergo autoxidation as the coating dries in air. Autoxidation is usually catalysed by the inclusion of drying agents (such as cobalt ions as, for example cobalt octoate, naphthenate or acetate) in the composition and they enable the copolymer macromolecules to crosslink

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either with each other or with other similarly
5 autoxidisable ingredients which may be optionally included
in the composition. Crosslinking is necessary for long
term water resistance which is poor if the amount of the
crosslinkable 3-allyloxy or 3-methallyloxy-2-hydroxypropyl
moiety is below 15 wt%. Optimum achievement of water
10 resistance occurs when the amount of these moieties is from
20 to 32 wt% of the weight of the partially esterified
carboxylic acid copolymer before neutralisation.

After partial esterification by the 3-allyloxy-2-
15 hydroxypropyl groups or their methallyl analogues the
copolymer should have enough remaining carboxylic acid
groups to give it an acid value of 25 to 60 (preferably 30
to 55) mg KOH/g unneutralised partially esterified
copolymer. Too low an acid value will not allow the
20 copolymer to have the ability to be made soluble by
neutralisation and too high a value destroys the water
resistance of the dried coatings.

The copolymerised carboxylic acid monomers or
25 anhydrides are derived by copolymerisation of acids or
anhydrides such as acrylic, methacrylic, itaconic,
crotonic, maleic and fumaric acids or their anhydrides.
Preferably the copolymerised carboxylic acid or acid
anhydride monomers represent from 20 to 40 mol % of the
30 partially esterified carboxylic acid polymer.

The copolymerised non-acid monomers are preferably
predominantly derived from hydrophobic unsaturated monomers
which have solubilities of less

than 6 wt% in pure water. However a minor proportion of the non-acid monomers may be hydrophilic especially if it is required to adjust the solubility of the ultimate neutralised partially esterified carboxylic acid copolymer. Examples of useful hydrophilic non-acid monomers include hydroxy ethyl acrylate, acrylamide, methacrylamide and the alkoxy (usually C_1 to C_4 alkoxy) polyethylene glycol methacrylates of various molecular weights.

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10 Preferably the hydrophilic non-acid monomers should not be present in amounts which cause the unneutralised partially esterified carboxylic acid copolymer to be soluble in de-mineralised water to the extent that a solution consisting of 10 wt%

15 unneutralised partially esterified copolymer and 90 wt% water after standing for 48 hours at 20°C has a nephelometer turbidity reading of at least 80 NTU. Preferably it should remain substantially insoluble at 20°C whilst still unneutralised.

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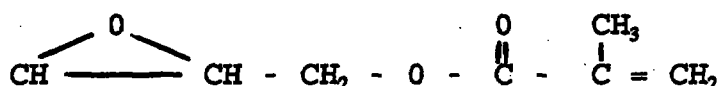
It is preferred to use hydrophobic non-acid monomers of the type conventionally used in making resins for the paint trade. The carboxylic acid copolymer may comprise just one such non-acid monomer such as methyl, ethyl or butyl acrylate but in general it has been found easier to obtain a better balance of properties when a combination of at least two non-acid monomers is used, one of which would give a homopolymer of high glass transition

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30 temperature (T_g), for example T_g above 30°C and one which would give a homopolymer of low T_g , for example T_g below -10°C. Monomers should be chosen which copolymerise at similar rates. T_g is calculated or measured according to the procedures hereinafter

described. Examples of non-acid monomers which give
 5 homopolymers of high Tg include methyl methacrylate, vinyl
 acetate and styrene. Examples of non-acid monomers which
 give homopolymers of low Tg include ethyl acrylate, methyl
 acrylate, butyl acrylate and the material commercially
 available from the Shell Chemical Company under the trade
 10 name "Vinyl Versatate" which is believed to be the vinyl
 ester of a mixture of branched chain acids which acids
 contain around 10 carbon atoms.

Less conventional non-acidic monomers include the
 15 adducts obtained by reacting glycidyl methacrylate which is



or its acrylate analogue with fatty acids derived from an
 20 unsaturated natural oil such as linseed oil fatty acid,
 tall oil fatty acids or soya bean oil fatty acid. Use of
 such monomers allows the weight of 3-allyloxy-2-
 hydroxypropyl moieties or the methallyl analogue present in
 the partially esterified copolymer to be reduced by up to
 25 15%.

Preferably the partially esterified carboxylic acid
 copolymer comprises from 0 to 55 mol % of the copolymerised
 non-acid monomer of the high Tg type and from 20 to 70 mol
 30 % of the non-acid monomer of the low Tg. type. Too much
 copolymerised monomer of the high Tg type or too little of
 the low Tg type leads to poor lapping whereas too much of
 the low Tg type increases the time needed to achieve touch

dryness. The partially esterified copolymer itself before neutralisation should preferably have a T_g of from -10°C to 15°C .

- 5 The weight average molecular weight of the partially esterified carboxylic acid copolymer (before neutralisation) is preferably from 10 000 to 100 000 when determined by the method hereinafter described. The most preferred range of weight
10 average molecular weights is from 15 000 to 75 000.

- The organic cosolvent assists the salt to dissolve and helps to control the viscosity of the coating composition as it dries in air which leads to
15 better application including better lapping. The cosolvent may also improve gloss. Accordingly it is preferred that the coating composition should contain at least 2 wt% (based on the weight of water and cosolvent) of organic cosolvent. The improvements
20 become less worthwhile with amounts of cosolvent beyond 25 wt% and so the preferred range of cosolvent concentrations is from 2 to 25 wt%.

- The organic cosolvent should be a liquid which
25 plasticises the partially esterified carboxylic acid copolymer and/or otherwise increases its solubility in water when neutralised. The cosolvent preferably has a boiling point of from 75 to 200°C at 1 bar absolute. Examples of useful cosolvents include
30 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 diolmonoisobutyrate, ethylene glycol, monopropyl, ~~mono~~butyl and ~~mono~~hexyl ethers,

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propylene glycol monomethyl, -ethyl, -propyl and -butyl ethers, diethylene glycol, dipropylene glycol, dipropylene glycol methyl ether, diethylene glycol ethyl ether, ethylene glycol monomethyl ether and most preferably
10 propylene glycol monomethyl ether (ie 1-methoxy-2-hydroxy propane (MHP)).

The coating compositions usually comprise from 10 to 50 wt% of the at least partially neutralised partially
15 esterified carboxylic acid copolymer (weighed before neutralisation) where the weight percentages are based on the weight of non-volatile material in the composition. Non-volatile content is determined according to the procedure of ASTM Test D 1210 - 79 the contents of which
20 are herein incorporated by reference. For partial gloss paints the preferred range is 5 to 25 wt% copolymer, for gloss paint it is 15 to 30 wt% copolymer and for varnishes it is 25 to 50 wt% copolymer.

25 It has further been discovered that carboxylic acid copolymers show less discolouration on ageing if the neutralising monovalent cations are Group 1 metal cations. The preferred cations are sodium, lithium or potassium.

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To obtain copolymers which dissolve well in aqueous liquids it is preferred that at least 75% (most preferably at least 90%) of the carboxylic acid groups present in the
10 copolymer be neutralised. An excess of cations may be present if an alkaline composition is required.

It has also been discovered that the gloss of dried coating obtained from the coating compositions containing
15 the salts of carboxylic acid copolymers can be improved by the inclusion in the composition of particles of insoluble solid organic polymeric material. Preferably the dispersion should be sufficiently stable to tolerate large amounts of organic solvent and in particular co-agulation
20 should not occur on adding to the dispersion enough MHP to give a dispersion comprising 33 wt% dispersed particles and 67 wt% of a mixture of equal weights of water and MHP.

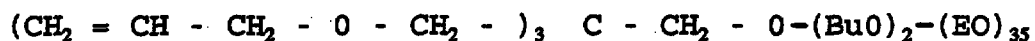
In order to obtain a highly stable aqueous dispersion
25 of the particles of the insoluble solid

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material in the presence of cosolvent it is necessary to chemically bond the material to molecules containing a hydrophilic moiety capable of at least helping to keep the particles dispersed. Such hydrophilic molecules should each contain a hydrophilic moiety and a moiety which bonds to the particulate material. Accordingly coating compositions according to this invention preferably also comprise dispersed particles of the insoluble solid material chemically bonded to hydrophilic molecules which at least help the particles to form a stable dispersion in the coating composition and which hydrophilic molecules each contain a hydrophilic moiety and a moiety which is bonded to the organic polymeric material. A preferred chemical bonding technique comprises choosing a copolymerisable hydrophilic monomer which can be chemically bonded into the organic polymeric material by copolymerisation with other monomers of the polymer. In effect this means that the hydrophilic monomers should comprise both a hydrophilic moiety and a polymerisable moiety. Preferred polymerisable moieties comprise carbon to

carbon double bonds such as allylic, acrylate or methacrylate groups.

5 Preferred hydrophilic groups include chains of poly(vinyl pyrrolidone), chains of polyoxazoline chains of polyamides especially polymethacrylamide or chains of poly(ethylene oxide) usually containing from 20 to 45 interconnected ethylene oxide molecules, such as those
10 found in alkoxy (preferably methoxy) polyethylene glycol methacrylates and the reaction product of pentaerythritol triallyl ether, butylene oxide and Example 1 of European Patent Specification EP-B-0 094 386, the contents of which are herein incorporated by reference. The reaction product
15 believed to have the formula:



where $(\text{BuO})_2$ is a chain containing two interconnected butylene oxide molecules and $(\text{EO})_{35}$ is a chain containing 35
20 interconnected ethylene oxide molecules.

The insoluble solid material to which the hydrophilic molecules are bonded and from which the particles are formed is preferably an organic polymeric material which is
25 not dissolved by the liquid component of the coating compositions. It is preferred to choose polymeric materials which are conventionally used by the paint trade. These are reviewed in Chapters 11 and 12 of the third edition of the book "introduction to Paint Chemistry and
30 Principles of Paint Technology" by GPA Turner and published in 1988 by

Chapman and Hall of London. The contents of these chapters are herein incorporated by reference. Examples of useful polymeric (including copolymeric) materials are the condensates such as polyamides, 5 polyesters and alkyd resins or the addition polymers made by polymerising or copolymerising monomers containing carbon to carbon double bonds such as styrene, vinyl toluene, ethylene, propylene, butylene, vinyl esters of saturated carboxylic acids 10 and the so called vinyl "Versatate", and unsaturated carboxylic acids such as acrylic, methacrylic, itaconic, crotonic, fumaric or maleic acids or their C_1 to C_4 esters.

Preferably the coating compositions comprise 15 from 10 to 50 wt% of the insoluble solid particles where the percentage is based on the combined weights of the particles and the anionic moieties of the salt. The size of the particles of organic polymeric material can sometimes be important. For example 20 very small particles may decrease the ability of the coating compositions to lap whilst very large particles can impair gloss instead of improving it. For these reasons it is preferred to choose particles having a number average diameter of not more than 25 1000nm and preferably from 25 to 600 nm.

In general where the insoluble solid particles are particles of organic polymeric material, the polymer will have a weight average molecular weight 30 of at least 30 000. The T_g of the polymers will usually be less than 100°C and preferably less than 25°C as calculated using the Fox equation with the procedure hereinafter described. The polymeric material may include moieties such as methylene

groups adjacent to carbon to carbon double bonds which undergo autoxidation as the coating composition dries in air.

5 This allows the polymeric material to crosslink either with itself or with autoxidisable moieties in other components of the coating composition such as the 3-allyloxy or 3-methallyloxy-2-hydroxypropyl groups in the carboxylic acid copolymer.

10 The coating compositions may additionally contain components conventionally used in making for example paints, varnishes or woodstains. Such
15 components include pigments, dyes, extenders, thickeners, fungicides, anti-skinning agents, flow improvers and drying agents. The coating compositions have also been found to have a good ability to soak into wood and so they are useful as
20 woodstains.

 The various measurement and assessment techniques referred to in this specification are defined as follows:

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Dynamic Viscosity Measurement Technique:

 The dynamic viscosities of the solutions of unneutralised partially esterified carboxylic acid copolymer in
30 1-methoxy-2-hydroxy propane (MHP) were measured using an oscillatory parallel plate rheometer.

 An oscillatory parallel plate rheometer consists of a rotatably oscillatable horizontal circular base plate spaced below a parallel circular top plate

mounted on a torque bar. In use the space between the plates is filled by the sample to be measured and the base plate is made to oscillate with a pre-determined amplitude of strain at a suitably high frequency. The sample viscoelastically couples the plates so that the oscillation of the base plate imposes a torque on the top plate. This imposed torque is balanced by an opposing torque applied to the top plate by the torque bar so as to keep the top plate stationary. The frequency of oscillation is gradually reduced. The applied torque needed to keep the top plate stationary also reduces with the reducing frequency of oscillation until eventually at lower frequencies it becomes constant. This constant value is a function of the dynamic viscosity of the sample and the geometry of the rheometer. Hence the rheometer can be calibrated to read dynamic viscosity directly.

For the purposes of this specification, the rheometer used is a Bohlin VOR rheometer supplied by Bohlin Reologi of Lund in Sweden and described in their brochure "The Bohlin VOR Rheometer" the contents of which are herein incorporated by reference. The plates used were 30 mm in diameter, spaced 1 mm apart and made from stainless steel. A 93.2 g cm torque bar was used together with a strain amplitude of 0.05 and a frequency range of from 20 to 0.01 Hertz. The measurement was done as follows:

Unneutralised partially esterified carboxylic acid copolymer was obtained as a solution in MHP which solution consisted of 90 wt% unneutralised partially esterified carboxylic acid copolymer and 10

wt% MHP. The solution was introduced between the plates of
5 the rheometer and heated to 60°C. It was maintained at
that temperature throughout the measurement operation.

Touch Dry Time Measurement:

The time taken for a freshly
10 applied coating to become dry to touch is measured by a
sand deposition procedure as follows:

A coating 50 to 60 μm thick is applied at 20°C and 50%
relative humidity to a horizontal planar dry coat of
15 conventional liquid gloss alkyd paint such as "Dulux"
(Registered Trade Mark) brilliant white liquid gloss which
had been allowed to dry at 20°C and 50% relative humidity
for at least 7 days. The coating is maintained at 20°C
throughout the measurement procedure. A hopper having a
20 small outlet in its base is filled with sand which then
trickles through the outlet. The hopper is caused to
traverse the coating at a speed of 25.4 mm/hour with sand
trickling onto the coating. Initially the sand sticks to
the coating which is still wet but as time passes, the
25 coating dries and there comes a point when the sand ceases
to stick to it. The time taken to reach this point is
regarded as the touch dry time for the purposes of this
specification. The point is easily detected by blowing the
loose sand from the fully dried coating so as to leave a
30 trail of stuck sand of a length from which the touch dry
time is calculated by dividing the length of the trail by
the speed of traverse.

"Dulux" (Registered Trade Mark) brilliant white liquid
5 gloss alkyd paint is available from the Paints Division of
Imperial Chemical Industries Plc of Slough England.

Water Spot Resistance Test:

The resistance of a freshly
10 applied coating to disfiguration by water is assessed as
follows:

Method A:

A coating 50 to 60 μm thick is applied to a dry coat
15 of a conventional alkyd paint obtained as in the touch dry
test above. The coating is allowed to dry for 24 hours at
20°C and 50% relative humidity. Then a 1 ml drop of water
is deposited onto it. The drop is removed after 15 minutes
and the coating is examined for disfiguration.

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Method B:

The procedure of Method A is followed up till and
including the deposition of the drop of water. However when
the drop has been deposited it is covered by a watch glass
25 and sample under test is allowed to stand at 20°C for two
hours. Then the glass is removed and the sample is
immediately wiped dry and examined for disfiguration.

Clarity/Turbidity Assessment Technique:

30 The clarities
or turbidities of solutions of salts of a fully neutralised
partially esterified carboxylic acid copolymer in a 4:1 (by
weight) mixture of water and 1-methoxy-2-hydroxy propane
(MHP) were assessed using a nephelometer.

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A nephelometer is an instrument designed to compare the light scattering ability of particles suspended in a liquid relative to the corresponding ability of a standard liquid containing no particles.

5 The nephelometer shines a horizontal beam of light through a sample under test and measures the amount of light scattered by the sample in a horizontal direction perpendicular to the beam. The extra amount of light scattered by the test sample relative

10 to the standard is given in nephelometer turbidity units (NTU). The smaller the reading in NTU, the less is the turbidity and hence the greater is the clarity of the solution.

15 For the purposes of this specification, the nephelometer used was Model 40-005 supplied by Turner Designs of Mount View, California USA and it is described in their brochure "Clear Water: Turbidity Nephelometry" Form 40-480, the contents of which are

20 herein incorporated by reference. The standard chosen was the 4:1 water/MHP mixture mentioned above for which the nephelometer was set to give a reading of 0.5 NTU at 20°C when operating in its x 10 mode. The measurement procedure used was as follows:

25 A solution of a salt of a fully neutralised partially esterified carboxylic acid copolymer was obtained which comprised of 25 wt% anionic moieties

30 of the salt and 75 wt% of the 4:1 (by weight) mixture of water and MHP where percentages are based on the combined weights in the solution of anionic moieties of the salt, water and MHP. A 20 ml sample of the solution was taken and maintained at 20°C for 48

hours and then its turbidity was measured on the nephelometer relative to the 4:1 water/MHP standard.

Solution Stability Assessment:

5 A solution comprising 33 wt% of anionic moieties
of a salt of a fully neutralised partially esterified
carboxylic acid copolymer and 67 wt% of a 3:1 (by
weight) mixture of water and MHP was allowed to stand
for 10 days in an incubator maintained at 40°C. The
10 solution was then examined by the unaided eye to see
whether any precipitation had occurred.

Weight Average Molecular Weight Measurement:

15 Weight average molecular weight is measured by making a solution consisting of 0.5 wt% copolymer in 99.5 wt% tetrahydrofuran and subjecting the solution to gel permeation chromatography using 300 mm linear
20 columns packed with 5 micron polystyrene gel supplied by Polymer Laboratories Ltd of Church Stretton, England. The results obtained are calibrated against a polystyrene standard.

25 Particle Diameter Measurement:

Number average particle diameter is measured by photon correlation spectroscopy using a Coulter nanosizer as supplied by Coulter Limited of Luton, England.

Discolouration (Yellowing) Test:

The discolouration or yellowing of a coating on ageing is assessed using spectrophotometry as follows:

A coating 100 μm thick was applied to a glass sheet and allowed to dry at 20°C. Using CIELAB 1931 Illuminant C (Northern Daylight), the reflectance of the coating at 20 nm intervals from 400 to 700 nm was measured and used to calculate a B (yellowing) value in accordance with the CIELAB system. The coating was then subjected to simulated ageing by storing it for 30 days in air and in the dark at 40°C after which it was allowed to cool to 20°C. The reflectance measurements were repeated and again used to calculate the CIELAB B value. The difference between the B values before and after ageing is a measure of the amount of yellowing which has occurred

15 Determination of Tg:

For the purposes of this specification, the Tg of a homopolymer is taken from Table 14 in the article "Concepts Involved in Designing Acrylic Copolymers in Solution" by D H Klein published in the "Journal of Paint Technology" Volume 42 No. 545 of June 1970, see pages 335 to 351, the contents of which are herein incorporated by reference or if the homopolymer is one which is not present in Klein's Table 14, then its Tg is taken from pages 143 to 192 (the contents of which are herein incorporated by reference) of Part III of the second edition of the "Polymer Handbook" edited by J Brandrup and E H Immergut and published in 1975 by John Wiley & Sons of New York or if the homopolymer is not present in Klein's Table 14 and the "Polymer Handbook", then its Tg is determined by compensation differential scanning calorimetry as described on pages 4 to 9 of the book "Thermal Characteristics of Polymeric Materials" edited by E A Turi and published

in 1981 by Academic Press INC (London) Ltd, the contents of which pages are herein incorporated by reference. The calorimetry should be performed on samples which have been heated isothermally at 100°C for 15 minutes. It should be mentioned however, that measurements of Tg are seldom accurate to more than +/- 5°C.

The Tg of the unneutralised copolymer and other copolymers is calculated using the Fox equation employing values for homopolymer Tg which are determined as above.

The invention is further illustrated by the following Examples of which Examples A to G are comparative.

EXAMPLES 1 TO 6
AND COMPARATIVE EXAMPLE A

Preparation of Partially Esterified Carboxylic Acid
5 Copolymers and Water-based Coating Composition
containing salts of the Copolymers:

10 Firstly a carboxylic acid copolymer consisting
of copolymerised acrylic acid monomer and various
copolymerised non-acid monomers was made by
copolymerising the monomers in 1-methoxy-2-hydroxy
propane (MHP). This was done by taking an amount of
15 MHP equal to either 25% (Examples 1, 3 to 5 and A) or
40 wt% (Examples 2 and 6) of the combined weights of
the acid and non-acid monomers and heating it under
reflux to 120 to 130°C. A mixture of the monomers
plus 5 wt% (based on the weight of the monomers) of a
20 free radical polymerisation initiator which was
tertiary butyl peroxy-2-ethyl hexanoate was added to
the refluxing MHP over a period of 3 hours during
which time copolymerisation occurred producing a
solution of carboxylic acid copolymer in MHP.
25 Refluxing was continued for an extra 15 minutes and
then a further 1 wt% of initiator was added over a
period of 1 hour to ensure completion of the
copolymerisation. The solution was then allowed to
cool to room temperature.

30

The solution was re-heated under reflux to 90 to
95°C and then allyl glycidyl ether and 1.5 wt% (based
on the weight of the ether) of 40 wt% solution in
water of an oxirane-ring opening catalyst (which was
benzyl trimethyl ammonium hydroxide) was added

dropwise over a period of 5 minutes. The solution was then heated to 130 to 135°C under reflux whereupon the allyl glycidyl ether partially esterified the carboxylic acid copolymer by
5 undergoing an addition reaction with some of the carboxylic acid groups in the carboxylic acid copolymer to produce a solution of a film-forming partially esterified carboxylic acid copolymer in MHP. Heating under reflux was continued until the
10 epoxide value of the solution had fallen to below 5mg KOH/g non-volatile contents of the solution and then the solution was allowed to cool to room temperature.

The amounts of acrylic acid, non-acid monomer
15 and allyl glycidyl ether used were chosen so as to produce unneutralised partially esterified carboxylic acid copolymers having a Tg of about -3°C and also the molecular and weight percentage compositions, acid values and weight average molecular weights
20 shown in Table 1. The weight percentage of the added allyl glycidyl moieties is based on the weight of the partially esterified carboxylic acid copolymer before neutralisation.

25 A small sample of the solution of partially esterified carboxylic acid copolymer was taken and MHP was removed by distillation at 1 bar absolute to produce a more concentrated solution consisting of 90 wt% of the copolymer and 10 wt%
30 MHP. The dynamic viscosity of the solution was measured by the technique hereinbefore described and the results are shown in Table 2.

The remainder of the solution of partially

esterified carboxylic acid copolymer was neutralised using just sufficient aqueous sodium hydroxide to neutralise all the remaining carboxylic acid groups so producing a fully neutralised water-based solution of the sodium salt of the partially esterified carboxylic acid copolymer.

A portion of the above salt solution was taken and water and MHP were added to it to produce a water-based coating composition comprising of 25 wt% anionic moieties of the salt and 75 wt% of a 4:1 (by weight) mixture of water and MHP, the percentages being based on the combined weights of the anionic moieties, water and MHP. The clarity/turbidity was assessed by measuring its turbidity according to the Clarity Assessment Technique hereinbefore described. The results are shown in Table 2.

A further portion of the salt solution was taken and water and MHP were added to it to produce a water-based solution this time comprising of 50 wt% anionic moieties and 50 wt% of a mixture of equal weights of water and MHP. Cobalt octoate was added to the solution (0.2 wt% cobalt ion based on the weight of the anionic moieties) and then the solution was divided into three sub-portions which were used respectively to determine touch dry time, water spot resistance (Method A) and discolouration on ageing all according to the techniques and procedures hereinbefore described. The results are shown in Table 2.

TABLE 1

Example	Mol % AA	Mol % copolymerised non-acid Monomer						Acid Value	Wt Av Mol Wt Part. Est. copol.
		EA	MMA	BA	MMMA	MEA	Sty		
1	29.5	24.5	24.5	-	-	-	-	21.5	63 000
2	29.5	24.5	24.5	-	-	-	-	21.5	18 500
3	30.5	-	24.5	21.9	-	-	-	22.2	53 000
4	30.0	24.9	22.5	-	0.8	-	-	21.8	36 000
5	29.9	29.9	18.7	-	-	4.8	-	21.7	57 000
6	29.6	24.6	18.4	-	-	-	5.9	21.5	57 000
A	29.4	-	49.1	-	-	-	-	19.8	25 000

* In all cases the wt% of 3AHP (based on the total weight of unneutralised copolymer) was 28.5.

Acid value is quoted in mg KOH/g unneutralised partially esterified carboxylic acid copolymer

3AHP 3-allyloxy-2-hydroxypropyl moiety

AA	Acrylic Acid	BA	Butyl Acrylate
EA	Ethyl Acrylate	MEA	Methoxy ethyl acrylate
MMA	Methyl Methacrylate		
MMMA	Methoxy polyethylene glycol methacrylate of molecular weight 350.		

TABLE 2

Example	Viscosity Pa. sec	Clarity/ Turbidity NTU	Sand Dry Times hours	Change in CIELAB B Value	Water Spot Resistance
1	175	52.2	2	2.8	Acceptable
2	45	16.1	2.25	3.0	Acceptable
3	88	21.7	2.5	3.2	Better
4	45	40.6	3.75	3.3	Better
5	48	62.8	2.25	3.1	Better
6	11	18.1	2.25	2.1	Acceptable
* A	925	-	-	-	-

* Would not lap

**EXAMPLES 7 TO 10
AND COMPARATIVE EXAMPLES B TO D**

5 Preparation of Coating Compositions comprising salts
made from partially esterified Carboxylic Acid
Copolymers of Widely Varying Acid Values.

10 Coating compositions were made up using the
general technique employed for Examples 1 to 6 except
that the ring opening catalyst was a propriety
chromium complex supplied as "Cordova Accelerator
15 AMC-2" by Cordova Chemi of Sacramento California. The
proportions of acid monomer, non-acid monomer and
allyl glycidyl ether used were chosen to give
unneutralised partially esterified copolymers having
a Tg of about -3°C and containing 10 mol % ethyl
20 acrylate and 34 wt% (25 mol%) 3-allyloxy-2-hydroxy
propyl moieties. The molar ratio of acrylic acid and
methyl methacrylate was varied as shown in Table 3 to
vary the acid value of the partially esterified
copolymer whilst maintaining its Tg at about -3°C .

25 Just enough of an aqueous solution of lithium
hydroxide was added to neutralise all the carboxylic
acid groups remaining in the copolymer after partial
esterification and then water and MHP were added
together with 0.2 wt% cobalt ion (as cobalt octoate
based on the weight of the anionic moieties) to
30 produce a coating composition comprising of 25 wt%
anionic moieties of the lithium salt and 75 wt% of a
4:1 (by weight) mixture of water and MHP. The coating
compositions were each in turn subjected to the
Solution Stability and Water Resistance Assessments
(Method A) as hereinbefore described and the results
are shown in Table 3.

TABLE 3

Example	Acid Value	Copolymer Composition mol % Wt%		Water Spot Resistance	Solution Stability
		EA 10 mol%, 3AHP 25 mol% (34wt%)	MMA mol%		
B	66	39	26	Shrivelled & Film Failure	Stable
7	46	36	29	Good	Stable
8	37	35	30	Good	Stable
9	30	34	31	Very Good	Stable
10	26	32	33	Very Good	Stable
C	17	31	34	-	Precipitated
D	11	29	36	-	Precipitated

Acid value is quoted in g KOH/g unneutralised partially esterified carboxylic acid copolymer.

It will be seen from Table 3 that coating compositions containing salts made from partially esterified carboxylic acid copolymers having acid values in excess of 60g KOH/g unneutralised copolymer were unacceptably sensitive to water whilst those made for copolymers having acid values below 25 did not have long term solution stability.

EXAMPLES 11 TO 16

AND COMPARATIVE EXAMPLES E TO G

Preparation of Coating Compositions comprising salts of partially esterified Carboxylic Acid Copolymers containing Varying Amounts of 3-allyloxy-2-hydroxypropyl Moiety.

Coating compositions were made according to the general procedure used for Examples 7 to 10. The proportions of acid monomer, non-acid monomer and allyl glycidyl ether used were chosen to give copolymers as specified in Table 4. Just sufficient aqueous sodium or lithium hydroxide was used to neutralise all the carboxylic acid groups remaining after partial esterification of the copolymer and then further water and MHP were added together with 0.2 wt% cobalt ion (as cobalt octoate and based on the weight of the anionic moieties) to produce a coating composition comprising 35 wt% anionic moieties of the salt and 65 wt% of a mixture consisting of equal weights of water and MHP. The solutions were examined by the unaided eye and the results are shown in Table 4 from which it will be seen that the amount of 3-allyloxy-2-hydroxy propyl moiety should not fall to 14 wt% or rise to 40 wt%. The preferred amounts are from 20 to 30 wt%.

TABLE 4

Example	Copolymer Composition				Acid Value	Cation	Water Spot Resistance
	Wt% 3AHP	Mol %					
		AA	EA	MMA			
F G	11	15	56	20	30	Na	*None
	14	17	50	21	33	Na	**Poor
11 12 13 14 15 16	17	19	45	21	36	Na	Acceptable
	20	22	40	22	34	Na	Better
	23	24	34	22	35	Na	Better
	26	26	29	23	37	Na	Better
	29	29	24	24	35	Na	Better
	34	35	10	30	36	Li	Acceptable
H	40	39	-	31	48	Li	***Poor

Acid Value is quoted in mg KOH/g unneutralised partially esterified carboxylic acid copolymer

* Film totally dissolved

** Almost total dissolution

*** Film shrivelled

EXAMPLES 17 to 19

5

Illustration of the Improved Gloss obtainable by Addition of Particulate Insoluble Solid Material.

Stable dispersions of insoluble organic polymeric material were made up for use in Examples 18 and 19.

Preparation of a Dispersion of Particles for use in Example 18:

The following charges were made up:

15

Charge A

Water	530g
"Levalan" (Registered Trade Mark) 208	7.5g
Surfactant as a solution consisting of 80wt% surfactant and 20 wt% water	
20 Borax	3.8g

Charge B

25

Methyl methacrylate	34.5g
Butyl acrylate	27.5g

Charge C

Water	6.75g
Tertiary butyl hydroperoxide	0.24g

30

Charge D

Water	12.0g
-------	-------

	Sodium metabisulphite	0.5g
--	-----------------------	------

Charge E

5	Water	6.0g
	Sodium metabisulphite	0.24g

Charge F

10	Water	6.8g
	Ammonium persulphate	1.35g

Charge G

15	Methyl methacrylate	320g
	Butyl acrylate	256g
	Surfactant as in Charge A	9.7g
	*Hydrophilic compound	32g

20 *The hydrophilic compound was the reaction product of pentaerythritol triallyl ether, butylene oxide and ethylene oxide reacted in the molar ratio 1:2:35 as described in EP-B-0 094 386.

25

Charge H

	Water	38.3g
	Sodium Metabisulphite	1.5g

30 Charge I

	Water	5.4g
	Ammonium persulphate	0.7

Charge J

Water	19g
Sodium metabisulphite	0.76g

5

Charge A was poured into a 2 litre flask fitted with a reflux condensor followed by Charges B and C in turn. The mixture obtained was warmed to 50°C and stirred for 15 minutes to emulsify the acrylic monomers. Charge D was added followed 10 minutes later by Charge E. Stirring was continued for twenty minutes during which time a pre-polymer seed was formed consisting of particles of number average diameter 70nm.

15

The flask was heated to 60°C and Charge F was added. Next Charges G and H were added dropwise and concurrently over a period of 150 minutes. Stirring was continued for a further 10 minutes and then Charge I was added followed immediately by dropwise addition of Charge J over 30 minutes. Finally stirring was continued for a further 30 minutes whereafter there was obtained a stable colloidal dispersion of pH 6.9 containing 52 wt% of solid particles of number average diameter 162nm. This dispersion was subsequently used to make up a paint for the purposes of Example 18.

The particles were particles of a copolymer comprising 52.9 wt% methyl methacrylate, 42.3 wt% butyl acrylate and 4.8 wt% hydrophilic moiety which copolymer had a Tg of 11°C and an indeterminate molecular weight owing to the presence of crosslinking. The dispersion was very stable in the presence of organic cosolvent and in particular it did not coagulate when mixed with MHP to produce a

second dispersion containing 33 wt% particles in a mixture of equal weights of water and MHP.

5 Preparation of a Dispersion of Particles for use in Example 19.

The following charges were made up:

Charge K

10

Distilled Water	939g
Ethanol	833g
Methoxy*poly(ethylene glycol) methacrylate	166g
(MeOPeGMA) as a solution of 30 wt%	
MeOPeGMA in a 4:1 (by weight) mixture	
of ethanol and water	

15

*The poly(ethylene glycol) chains had a number average molecular weight of 2000

20

Charge L

Methyl methacrylate	57.5g
2-ethyl hexyl acrylate	67.5g
Azobis-isobutyronitrile	2.5g

25

Charge M

Methyl methacrylate	457g
2-ethyl hexyl acrylate	536g
MeOPeGMA	46g
Ethanol	37g
Azobis-isobutyronitrile	14.4g

30

Charge N

	Methyl methacrylate	152g
	2-ethyl hexyl acrylate	179g
5	Azobis-isobutyronitrile	4.8g

Charge K was poured into a 3 litre flask fitted with a reflux and the mixture obtained was stirred and heated to 81°C. Charge L was added and stirring and heating under reflux was continued for 30 minutes during which time a pre-polymer seed was formed of number average particle size 95nm.

Next, Charge M was added to the returning condensed ethanol dropwise over a period of 3 hours followed by the dropwise addition over 1 hour of Charge N. Heating to 81°C and stirring were continued for a further 30 minutes. 10g of the liquid returning from the condensor to the flask were removed and used to dissolve a further 3g of azo-isobutyronitrile. The solution obtained was added to the flask whereafter heating and stirring was continued for a further 30 minutes. Lastly, enough ethanol was distilled off to give a dispersion of pH 6.9 containing 51 wt% of solid particles of number average diameter 231nm. This dispersion was subsequently used to make up a paint for the purposes of Example 19.

The particles were particles of a copolymer comprising 43.2 wt% methyl methacrylate, 50.7 wt% 2-ethylhexyl acrylate and 6.2 wt% MeOPeGMA which copolymer had a Tg of -15°C and a weight average molecular weight of 68,000. The dispersion was very stable in the presence of organic cosolvent and in

particular it did not coagulate when mixed with MHP to produce a second dispersion containing 33 wt% particles in a mixture of equal weights of water and MHP.

5 Preparation of Paints for Examples 17, 18 and 19:

The following charges were made up:

10 Charge O

A solution consisting of 42.5 wt% MHP solvent and 57.5 wt% of an unneutralised partially esterified carboxylic acid copolymer made according to the
15 procedure of Example 2.

Charge P

A blend consisting of 51g of Charge O and 41g of
20 the dispersion of particles made for use in Example 18.

Charge Q

25 A blend consisting of 51g of Charge O and 41g of the dispersion of particles made for use in Example 19.

30 61.5g of titanium dioxide pigment were added to 60g of Charge O and subjected to high speed stirring to produce a dispersion of particles of titanium dioxide. Next either 51g of Charge O (Example 17) or the whole of Charge P (Example 18) or the whole of Charge Q (Example 19) was stirred into the blend together with 1.7g cobalt octoate drying agent.

Finally 106g of water was stirred into blends to give a gloss paint of viscosity 3.4 to 3.6 poise as measured on the ICI Cone and Plate Viscometer.

5 The paints were each applied to a glass plate at 20°C and relative humidity of 50% and allowed to dry for 24 hours.

10 The specular gloss of the dried coatings were then measured according to ASTM Test D523 using light reflected at an angle of 20°C to the normal to the dried coating. The following results were obtained:

	Example	Gloss
	17 (no particles)	63
15	18 (with particles)	73
	19 (with particles)	74

20 It was also found that paints made according to Examples 18 and 19 had improved water spot resistance (Method B).

EXAMPLE 20

25 The procedure of Example 2 was repeated except that the partially esterified carboxylic acid copolymer was neutralised using aqueous ammonia instead of sodium hydroxide. The coating composition obtained was subjected to the Discolouration Test hereinbefore described. The change in CIELAB B value
30 obtained was 6.7 as compared with 3.0 when the neutralising ion was sodium.

The coating compositions exemplified are

suitable for use in paints which lap well when evaluated according to the procedure hereinbefore described.

CLAIMS

5 1. A water-based autoxidisable air-drying coating
composition suitable for application at ambient
temperatures which comprises water, 0 to 50 wt% organic
cosolvent (based on the weight of water and cosolvent) and
a salt of monovalent cations and partially esterified
10 carboxylic acid film-forming copolymer at least partially
neutralised by the cations wherein

a) the partially esterified carboxylic acid copolymer
comprises

15 (i) copolymerised acid monomer/s derived by
copolymerisation of at least one unsaturated
carboxylic acid monomer or its anhydride and
which copolymerised monomer/s provide carboxylic
acid groups to the copolymer,

20

(ii) copolymerised non-acid monomer/s and

(iii) 15 to 38 wt% (based on the weight of the
partially esterified carboxylic acid copolymer
25 before neutralisation) of 3-allyloxy-2-
hydroxypropyl moieties or their 2-methylallyl
analogue (that is to say $-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{CH}_2-$
 $\text{CR}=\text{CH}_2$ where R is H or CH_3) by which the
carboxylic acid copolymer is partially
30 esterified.

b) the acid value of the partially esterified carboxylic
acid copolymer before neutralisation is from 25 to 60 mg
KOH/g unneutralised partially esterified copolymer and

35



- c) the nature of the partially esterified carboxylic acid copolymer is such that the copolymer gives a solution viscosity of from 1 to 500 pa.sec when measured at 60°C on a solution consisting of 90 wt% unneutralised partially esterified carboxylic acid copolymer and 10 wt% 1-methoxy-2-hydroxy propane using an oscillatory parallel plate rheometer.
- 10
2. A coating composition according to Claim 1 wherein the composition comprises from 2 to ²⁵~~24~~ wt% (based on the weight of water and cosolvent) of organic cosolvent.
- 15
3. A coating composition according to Claim 1 or Claim 2 wherein the composition contains 1-methoxy-2-hydroxy propane as an organic cosolvent.
4. A coating composition according to any one of Claims 1
- 20 to 3 wherein the salt comprises enough monovalent cation to neutralise at least 75 wt% of the non-esterified carboxylic acid groups of the partially esterified carboxylic acid copolymer.
- 25
5. A coating composition according to Claim 4 wherein the partially esterified carboxylic acid copolymer is fully neutralised.
6. A coating composition according to any one of Claims 1
- 30 to 5 wherein the monovalent cations are Group 1 metal cations.



7. A coating composition according to any one of Claims 1 to 6 wherein the partially esterified carboxylic acid copolymer comprises from 20 to 40 mol% of copolymerised carboxylic acid or acid anhydride monomer/s.
8. A coating composition according to any one of Claims 1 to 7 wherein the copolymerised acid monomer/s are derived by copolymerisation of monomer/s chosen from acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid and fumaric acid and their anhydrides.
9. A coating composition according to any one of Claims 1 to 8 wherein the partially esterified carboxylic acid copolymer comprises from 20 to 70 mol% copolymerised non-acid monomer/s of the type which would produce a homopolymer having a Tg (Glass Transition Temperature) of below -10°C.
10. A coating composition according to Claim 9 wherein the non-acid monomer/s are chosen from methyl, ethyl and butyl acrylates and the vinyl esters of a mixture of branched chain acids containing 10 carbon atoms.
11. A coating composition according to any one of Claims 1 to 10 wherein the partially esterified carboxylic acid copolymer comprises up to 55 mol% of copolymerised non-acid monomer/s of the type which would produce a homopolymer having a Tg of above 30°C.
12. A coating composition according to Claim 11 wherein the non-acid monomer/s are chosen from methyl methacrylate, vinyl acetate and styrene.



13. A coating composition according to any one of Claims 9
5 to 12 wherein the non-acid monomers also include a minor
proportion of hydrophilic monomer/s.

14. A coating composition according to Claim 13 wherein the
hydrophilic monomer/s are chosen from hydroxyethyl
10 acrylate, acrylamide, methacrylamide and alkoxy
polyethylene glycol methacrylates.

15. A coating composition according to any one of Claims 9
to 14 wherein the non-acid monomers also include at least
15 one adduct of glycidyl acrylate or methacrylate with a
fatty acid derived from an unsaturated natural oil.

16. A coating composition according to any one of Claims 1
to 15 wherein the partially esterified carboxylic acid
20 copolymer if fully unneutralised would have a Tg of from
-10°C to 15°C.

17. A coating composition according to any one of Claims 1
to 16 wherein the nature of the partially esterified
25 copolymer which provides the anionic moieties to the salt
is such that where the copolymer is fully neutralised by
sodium cations, the salt so produced is soluble at least to
the extent that a solution comprising 25 wt% anionic
moieties of the salt and 75 wt% of a mixture of equal
30 weights of water and 1-methoxy-2-hydroxy propane (MHP)
(where the percentage is based on the combined weights of
anionic moieties, water and MHP) appears clear to the
unaided eye after the solution has stood for 48 hours at
20°C.



18. A coating composition according to Claim 17 wherein the
5 fully neutralised sodium salt is soluble at least to the
extent that the solution comprising 25 wt% anionic moieties
and 75 wt% of the mixture of water, and MHP after standing
for 48 hours at 20°C has a nephelometer turbidity reading
of less than 80 nephelometer turbidity units.
- 10 19. A coating composition according to any one of Claims 1
to 18 wherein the composition also comprises dispersed
particles of insoluble solid organic polymeric material.
- 15 20. A coating composition according to Claim 19 wherein the
composition contains from 10 to 50 wt% of the particles
based on the combined weights of the particles and anionic
moieties of the salt.
- 20 21. A coating composition according to Claim 19 or Claim 20
wherein the insoluble solid organic polymeric material has
a weight average molecular weight of at least 30 000.
- 25 22. A coating composition according to any one of Claims 19
to 21 wherein the number average particle diameter of the
particles of organic polymeric material is from 25 to
1000 nm.
- 30 23. A coating composition according to any one of Claims 19
to 22 wherein the insoluble solid organic polymeric
material has a Tg of below 100°C.
- 35 24. A coating composition according to any one of Claims 19
to 23 wherein the insoluble solid organic polymeric
material also comprises autoxidisable moieties.
25. A coating composition according to any one of the
Claims 19 to 24 wherein the insoluble solid organic
polymeric material comprises copolymerised hydrophilic



monomers derived from hydrophilic monomers comprising a
5 polymerisable moiety.

26. A coating composition according to Claim 25 wherein the
copolymerised hydrophilic monomers are derived from
hydrophilic monomers containing carbon to carbon double
10 bonds.

27. A coating composition according to Claim 26 wherein the
hydrophilic molecules are chosen from alkoxy polyethylene
glycol methacrylates or the reaction product of
15 pentaerythritol triallyl ether, butylene oxide and ethylene
oxide.

28. A partially esterified carboxylic acid film-forming
copolymer wherein
20 a) the partially esterified carboxylic acid copolymer
comprises

(i) copolymerised acid monomer/s derived
by copolymerisation of at least one unsaturated
25 carboxylic acid monomer or its anhydride and
which copolymerised monomer/s provide carboxylic
acid groups to the copolymer,

(ii) copolymerised non-acid monomer/s and
30

(iii) 15 to 38 wt% of 3-allyloxy-2-hydroxypropyl
moieties or their 2-methylallyl analogue by which
the carboxylic acid copolymer is partially
esterified,
35

b) the acid value of the partially esterified carboxylic
acid copolymer is from 25 to 60 mg KOH/g partially
esterified copolymer and



c) the nature of the partially esterified carboxylic acid
5 copolymer is such that the copolymer gives a solution
viscosity of from 1 to 500 Pa.sec when measured at 60°C on
a solution consisting of 90 wt% unneutralised partially
esterified carboxylic acid copolymer and 10 wt% 1-methoxy-
2-hydroxy propane using an oscillatory parallel plate
10 rheometer.

29. A copolymer as claimed in Claim 28 when at least
partially neutralised by monovalent cations.

15 30. A copolymer as claimed in Claim 29 wherein the cations
are Group 1 metal cations.

31. A copolymer as claimed in any one of Claims 28 to 30
wherein the partially esterified carboxylic acid copolymer
20 comprises from 20 to 40 mol% of copolymerised carboxylic
acid or acid anhydride monomers.

32. A copolymer according to any one of Claims 28 to 30
wherein the copolymerised acid monomers are derived by
25 copolymerisation of monomers chosen from acrylic acid,
methacrylic acid, itaconic acid, crotonic acid, maleic acid
and fumaric acid and their anhydrides.

33. A copolymer as claimed in any one of Claims 28 to 32
30 wherein the copolymer comprises from 20 to 70 mol%
copolymerised non-acid monomer/s of the type which would
produce a homopolymer having a Tg of below -10°C.

34. A copolymer according to Claim 33 wherein the non-acid
35 monomer/s are chosen from methyl, ethyl and butyl acrylates
and the vinyl esters of a mixture of branched chain acids
containing 10 carbon atoms.

35. A copolymer according to any one of Claims 28 to 34



wherein the copolymer comprises from 0 to 55 mol% of
5 copolymerised non-acid monomer/s of the type which would
produce a homopolymer having a Tg of above 30°C.

36. A copolymer according to Claim 35 wherein the non-acid
monomer/s are chosen from methyl methacrylate, vinyl
10 acetate and styrene.

37. A copolymer according to any one of Claims 28 to 36
wherein the non-acid monomers also include a minor
proportion of hydrophilic monomers.
15

38. A copolymer according to Claim 37 wherein the
hydrophilic monomer/s are chosen from hydroxyethyl
acrylate, acrylamide, methacrylamide and alkoxy
polyethylene glycol methacrylates.
20

39. A copolymer according to any one of Claims 28 to 38
wherein the non-acid monomer/s include at least one adduct
of glycidyl acrylate or methacrylate with a fatty acid
derived from an unsaturated natural oil.
25

40. A copolymer according to any one of Claims 28 to 39
wherein the copolymer if fully unneutralised would have a
Tg of from -10°C to 15°C.

30 41. A copolymer according to any one of Claims 28 to 40
wherein the nature of the partially esterified copolymer is
such that where the copolymer is fully neutralised by
sodium cations, the salt so produced is soluble at least to
the extent that a solution comprising 25 wt% anionic
35 moieties of the salt and 75 wt% of a mixture of equal
weights of water and 1-methoxy-2-hydroxy propane (MHP)
(where the percentage is based on the combined weights of
anionic moieties, water and MHP) appears clear to the



unaided eye after the solution has stood for 48 hours at
5 20°C.

42. A copolymer according to Claim 41 wherein the fully
neutralised sodium salt is soluble at least to the extent
that the solution comprising 25 wt% anionic moieties and 75
10 wt% of the mixture of water and MHP after standing for 48
hours at 20°C has a nephelometer turbidity reading of less
than 80 nephelometer turbidity units.
