

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
16 December 2004 (16.12.2004)

PCT

(10) International Publication Number
WO 2004/108847 A1

- (51) International Patent Classification⁷: **C09D 201/02**, 151/00, 5/16
- (21) International Application Number: PCT/EP2004/005758
- (22) International Filing Date: 26 May 2004 (26.05.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
0312916.0 5 June 2003 (05.06.2003) GB
0329415.4 19 December 2003 (19.12.2003) GB
- (71) Applicant (for all designated States except US): **IMPERIAL CHEMICAL INDUSTRIES PLC** [GB/GB]; 20 Manchester Square, London W1U 3AN (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **GOODALL, Glenn, William** [GB/GB]; 99 Kirk Meadow, Bretton, Peterborough, Cambridgeshire PE3 8JJ (GB). **TAYLOR, Philip, Louis** [GB/GB]; Heathlands, 74 Stomp Road, Burnham, Buckinghamshire SL1 7LT (GB).
- (74) Agent: **FRANGO, Andrew**; ICI Paints, ICI Group Intellectual Property, P.O. Box 1883, Wexham Road, Slough PDO, Berkshire SL2 5FD (GB).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: A MODIFIED BINDER POLYMER FOR COATING COMPOSITIONS

(57) Abstract: A film-forming binder polymer for a coating composition such as a paint, varnish or woodstain where the polymer is modified by the presence of bonded moieties derived from plant gum, particularly plant fibre gum obtainable from plant fibre, especially corn fibre gum and more particularly moieties derived from proteo-xylans and/or furanose. The modified binder polymer minimises the need to use coalescing solvents without producing poor dried paint coatings which fail the scrub resistance tests also improves the opacity of the dried coating composition.

WO 2004/108847 A1

A MODIFIED BINDER POLYMER FOR COATING COMPOSITIONS

This invention relates to a modified film-forming binder polymer for a coating composition and to coating compositions containing the modified polymer. The modified polymer is especially useful in architectural coating compositions such as paints, varnishes or woodstains which can be applied
5 by brush, roller or pad at ambient temperatures of say 0 to 30°C to surfaces associated with buildings, furniture or fittings found in or around buildings. For brevity, all such architectural coating compositions will be referred to as “paints”.

10 All aqueous architectural paints contain film-forming binder polymer. As a coating of liquid paint dries on a surface, this film-forming binder polymer

serves to form a film (i.e. a dried coat) of paint which bonds to the surface and also binds together all the non-volatile components of the paint including particularly any opacifiers, pigments and extenders present.

5 A wide variety of conventional film-forming binder polymers are available, but those most commonly used in aqueous architectural paints are of three broad types obtained from mono-ethylenically unsaturated monomers and known colloquially as the "acrylics", the "vinyls" and the "styrenics". The "acrylics" are usually copolymers of at least two alkyl esters of one or more
10 mono-ethylenically unsaturated carboxylic acids (e.g. methyl methacrylate-butyl acrylate copolymer) whilst the "vinyls" usually comprise copolymers of a mono-vinyl ester of a saturated carboxylic acid and at least one of either an acrylic monomer or a different mono-vinyl ester. The "styrenics" are copolymers containing styrene (or a similar mono-vinyl aromatic
15 monomer) together with a copolymerisable monomer which is usually an acrylic.

Such film-forming binder polymers may be produced as solution copolymers or dispersion copolymers in a carrier liquid. Solution
20 copolymers are substantially dissolved in the carrier liquid whereas dispersion copolymers are produced as discrete particles in the carrier

liquid. The solventborne or aqueous dispersions of particles require stabilisers, sometime referred to as emulsifiers or surfactants, to prevent the particles from flocculating and forming a sediment, thereby improving the storage and shear stability of the dispersion. The carrier liquid may be organic solvent or an aqueous medium. Typically the carrier liquid used to make a solution copolymer is a liquid which is a good solvent for the copolymer concerned such that the copolymer is substantially dissolved in it. Where the carrier liquid is aqueous, at least 50% by weight of the liquid is water with the remainder being water compatible organic solvent or solvent mixture.

Such solution or dispersion copolymers useful as film forming binder polymers, whether solventborne or waterborne can be made by well-known solution polymerisation or emulsion polymerisation methods respectively.

Paints containing aqueous dispersions of particles of conventional film-forming binder polymers apply well to surfaces at warmer temperatures of say above 10°C but if they are applied at low temperatures, the dried coats of paint formed are prone to cracking and consequently poor scrub resistance. Cracking occurs because the low temperatures impede the coalescence of the binder polymer particles into a film. Coalescence can be improved by adding organic so-called "coalescing solvents" to the paint

formulation and typical of such organic solvents are ethylene glycol, propylene glycol, benzyl alcohol and the proprietary solvent called "Texanol" which is trimethylpentane diol isobutyrate. Nowadays such solvents are considered to be environmentally unfriendly and so an alternative solution to the cracking problem has been to use binder polymers having much lower glass transition temperatures (Tg) despite the known disadvantages of such low Tgs. The first disadvantage is a reduction in scrub-resistance. The second disadvantage is that the tackiness associated with newly applied dried coats of paint persists for longer. Glass transition temperature, Tg, is defined in European Patent Specification EP 0 425 085A, the contents of which are herein incorporated by reference.

Opaque paints often contain particulate pigments such as titanium dioxide in the form of rutile as an opacifying white pigment. The rutile particles are coated with other oxides to minimise any tendency for rutile to promote light induced degradation and so the rutile is expensive. Rutile also detracts from the scrub-resistance of a dried coat of paint if used in a high concentration in the paint formulation.

The amount of pigment in a dry paint film is an important feature as it can affect, for example, the final colour, opacity, hardness and scratch resistance

of the dried paint. It is usually expressed as the volume of the pigment contained in the dry film compared with the total volume of the dried paint (including binder). This ratio is generally referred to as the Pigment Volume Concentration or PVC of the paint and expressed as a percentage.

5 Other non-film forming particulate materials such as fillers and extenders, for example China Clay, may be included in the calculation to give the total PVC, expressed here as PVC(total) to distinguish it from PVC(TiO₂) which refers to the PVC resulting only from the titanium dioxide content of the paint.

10

Opacifying pigments such as titanium dioxide can be expensive as well as having detrimental effects on paint properties such as scrub resistance and durability. Any improvement in opacity of the paint can be exploited by reducing the cost of the paint or improving the opacity so that fewer coats
15 of paints are required. This is particularly important in pastel shades and whites as such colours are usually of low opacity.

It is an object of this invention to provide a modified film-forming binder polymer for a coating composition which at least minimises and usually
20 avoids the need for the coating composition to contain an organic coalescing solvent without inducing film cracking or creating poor scrub-

resistance and persistent tackiness in a dried coat of paint. An alternative object is to improve the opacity of coating compositions. A further alternative object is to promote the opacifying and pigmenting efficiency of titanium dioxide, especially rutile so that less of it is needed in a formulation to achieve a given opacity. A still further object of the invention is to provide coating compositions containing the modified film-forming binder polymer.

Accordingly, this invention provides a film-forming binder polymer for a coating composition wherein the polymer is modified by the presence of bonded moieties, preferably proteo-xylans and/or furanose moieties, obtainable from plant gums.

Preferably, the amount of modification on a weight basis of modified binder is from 0.1% to 15%, more preferably from 1% to 10%.

The term bonded is intended to include not only the situation where the plant gum moieties and the film forming binder polymer are chemically combined by, for example covalent bonds, but also when they exist as an intimate mixture. Preferably the bonded moieties are chemically attached, more preferably by covalent bonds, to the binder polymer. Where the

modified film forming binder polymer is a dispersion, it is preferred that the majority, preferably all of the particles are each substantially comprised of both the binder polymer and the plant gum moieties whether chemically combined or as a mixture. Even more preferably, the particles are of the
5 core shell type.

It has been found that coating compositions containing the modified binder polymer require minimal and usually zero amounts of an organic coalescing solvent yet do not suffer from significant film cracking, poor scrub
10 resistance or excessively persistent tackiness in a dried coat of the composition. Also, the opacity of coating compositions is improved.

Suitable plant gums include those that exude from plants, usually trees with damaged bark. A suitable such gum is gum arabic, produced by the acacia
15 tree. Alternatively and additionally suitable plant gums are obtainable from plant fibre which form the fibrous parts of plants. Typically, the fibrous parts originate from the husk or seed case but any plant fibre material will do. Useful plant gums containing moieties suitable for modifying the binder polymer are obtainable from the fibrous material of various plants,
20 including corn or maize, wheat, oats, barley, rice and sugar beet. Plant gum obtainable from sugar beet is also known as araban.

In order to obtain plant gums from plant fibres, the fibres must undergo chemical treatment. United States Patent specification US 6,147,206 published 14 November 2000, the content of which is herein incorporated
5 by reference, describes such a process for extracting gum from corn fibre, although the teaching contained therein can be used to extract plant gum from other plant fibre material too.

10 A summary of the process disclosed in US 6,147,206 is as follows.
Crude corn fibre is obtained as a by-product from the wet or dry milling of corn, a process used to extract starch. The crude corn fibre obtained from the milling process contains some 20% by weight of starch. This is removed by one of two methods: slurring the fibre in water at approximately 7 wt%
15 solids and heating to 90°C followed by treatment with a thermally stable alpha amylase enzyme for at least 1 hour. A suitable amount of the enzyme is about 1 wt % on fibre solids. Following this, the fibre is filtered through a screen or a horizontal decanter to get rid of the solubilised starch and rinsed with fresh water to yield the destarched fibre. Alternatively, the fibre is
20 slurried with water and cooked in a continuous cooker where it is exposed to steam for a few seconds thereby solubilising the starch. The fibre is rinsed

with fresh water and filtered using a series of screens or a horizontal decanter to yield the destarched fibre. The destarched fibre from either process, now containing 2% or less by weight of starch, is slurried in water again and the pH raised to 11.5 with sodium hydroxide or calcium

5 hydroxide. Sodium hydroxide is preferred. The temperature is raised to 95°C and an aqueous solution of hydrogen peroxide (33%) is added at about 10 wt% calculated on the solids of the destarched fibre. The temperature of the slurry is maintained at 95°C for about an hour, after which time it is filtered at the high pH through a horizontal decanter to remove the corn

10 fibre residue, now substantially devoid of corn fibre gum. The alkaline liquid contains the corn fibre gum. The pH of the alkaline liquid is reduced to 4.5 using hydrochloric acid whereupon a precipitate is formed which is filtered using a vacuum drum coated with diatomaceous earth. The precipitate is discarded and the resulting solution spray dried to yield a dry

15 corn fibre gum useful for modifying film forming binder polymer.

Suitable plant gums include mixtures comprising polysaccharides, proteins and ash, an insoluble material. The relative amounts, by weight, of these materials vary from 65 to 85:0.5 to 35:0 to 15 respectively, varying

20 according to the precise process used to obtain the plant gum. Preferably the

amount of ash is below 5% and the protein from 2 to 15%, the remainder being polysaccharide.

The polysaccharides found in plant gums are composed of various
5 monosaccharides, including glucose, galactose, mannose, xylose, arabinose
(a 1:1 mixture of pyranose and furanose), rhamnose and glucuronic acid.
However, some of the protein is thought to be covalently bonded to the
polysaccharides to form protein-polysaccharide adducts known as a proteo-
xylan. Such proteo-xylans are effective surface-active agents which makes
10 plant gums containing them particularly useful in providing aqueous
dispersions of binder polymers. Preferably, at least some of the plant gum is
proteo-xylan; more preferably substantially all of it is.

Corn fibre gum is a well known product described in the paper 'Potential
15 New Uses for Corn Fiber' given by K B Hicks et al during the Proceedings
of the Corn Utilization and Technology Conference, Kansas City, USA held
on the 2nd to 5th June 2002 and published by the National Corn Growers
Association and Corn Refiners Association, see pages 122 to 127. The
content of these pages is herein incorporated by reference.

Typical corn fibre gum comprises approximately 80% by weight polysaccharide, 5% protein and 15% ash; the polysaccharide component consisting of galactose, xylose, arabinose and glucuronic acid.

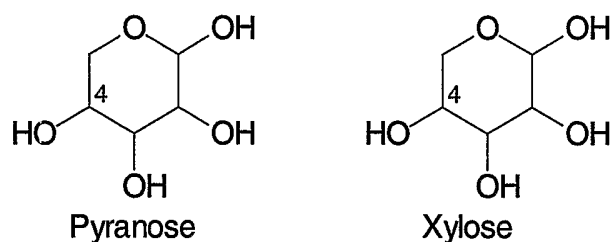
5 Plant gum obtainable from corn fibre, gum arabic and/or sugar beet fibre has been found to be particularly useful in providing aqueous dispersions of modified polymer particles, especially where the particles comprise binder polymer. Such dispersions are very stable, resisting sedimentation, and produce very little fouling of the polymerisation reactor during
10 manufacture. It is thought that this may be due to the presence of proteo-xylans in these gums.

Preferably, the binder is modified by the presence of bonded moieties obtainable, more preferably obtained from corn fibre gum. Preferably, the
15 corn fibre gum is used at a level of from 0.1wt % to 10wt%, even more preferably from 1wt% to 5wt% and most preferably from 2wt% to 4wt%, based on the total binder polymer.

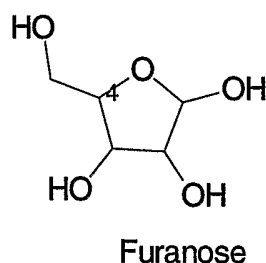
Galactose and glucuronic acid are present in a weight ratio of about 2:1.
20 Pyranose and xylose have the structural formulae, differing only at the carbon 4 position where pyranose has the hydroxyl group above the ring

whereas in xylose the hydroxyl group is below the ring. Note that the protons on the ring carbons have been omitted for simplicity.

5



Furanose has the structural formula shown below where there is a very labile hydrogen atom at carbon 4 which is thought to readily take part in
10 chemical reactions including bonding to conventional monomers during



polymerisation processes in which they form binder polymers. The lability of the hydrogen at position 4 is described in an article by Gilbert et al. on pages 1565 to 1572 of the Perkin Transactions (Volume 2) of the Journal of
15 the Chemical Society of 1998, the contents of which pages are herein incorporated by reference. It is thought that the ability of furanose to take part in such reactions helps to graft the polysaccharide and or proteo-xylans to the binder polymer.

The examples of suitable mono-ethylenically unsaturated monomers used to make conventional (that is unmodified) polymers are also suitable for making the binder polymers modified with corn fibre gum. Such monomers

5 include:

a) "acrylics" such as alkyl (especially methyl, ethyl, ethylhexyl and n-butyl) esters of unsaturated carboxylic acids such as acrylic or methacrylic or fumaric acids or maleic anhydride,

10 b) "vinyls" such as mono-vinyl esters (especially vinyl acetate or vinyl "Versatate"¹) and

c) "styrenics" which are usually styrene but which can be other monovinylidene aromatics such as vinyl toluene or vinyl pyridine and which are usually copolymerised with comonomers such as the ethyl or ethylhexyl or butyl acrylics mentioned above.

15 Various mono-ethylenically unsaturated acid or acid anhydride monomers may be copolymerised with the binder monomers to increase the hydrophilic character of the binder polymer in alkaline solutions. This is especially advantageous as it serves to increase the stability of the aqueous dispersions. However the acid comonomers usually do not exceed 7 mol %

¹ Vinyl "Versatate" is the vinyl ester of so-called "Versatic" acid which is a mixture of aliphatic monocarboxylic acids each containing an average of 9, 10 or 11 carbon atoms and is commercially available from the Shell Chemical Company of Carrington, England.

of the total monomers for otherwise the binder polymer becomes too hydrophilic to retain acceptable scrub-resistance.

Suitable acids include unsaturated carboxylic acids and in particular acrylic or methacrylic acids and unsaturated acid anhydrides include maleic anhydride. Acids or their anhydrides may allow some bonding of the binder polymer by ester formation to other hydroxylic moieties in the corn fibre gum in addition to the bonding to furanose by means of labile hydrogen.

10 It is desirable to choose combinations of monomers which include a sterically bulky monomer so as to result in binder polymers in which the chain moieties have a Tg of below 77°C and preferably below 52°C. Even more preferably the Tg is from -20°C to 27°C and most preferably from -10°C to 10°C. Preferred “acrylic” binder copolymers include copolymers of methyl methacrylate with butyl acrylate or 2-ethylhexyl acrylate as
15 sterically bulky monomers and optionally copolymerised with up to 7 mol % acrylic or methacrylic acid. Preferred “vinyl” binder copolymers include copolymers of vinyl acetate with a bulky monomer which is usually vinyl “Versatate” or bulky acrylic monomer as above plus the same optional acid
20 comonomers. Preferred “styrenic” binder copolymers include copolymers of styrene with butyl acrylate or 2-ethylhexyl acrylate serving as the bulky

monomers with optionally up to 7 mol % acid comonomers as above. T_g will be increased unacceptably by excessive crosslinking and so it is essential not to incorporate more than 7 wt % of a conjugated diene into the binder polymer and it is very much preferred to avoid any such diene.

5

Preferably the film forming binder polymer is carried in aqueous medium. This reduces the organic solvent lost to the atmosphere when a paint based on such a binder is used thereby minimising unpleasant odours, especially when painting in an enclosed space. More preferably it is an aqueous
10 dispersion of polymer particles and most preferably it is made by an emulsion polymerisation process.

If copolymerisation at superatmospheric pressures is commercially tolerable, the hydrophilic nature of the binder polymer can be adjusted
15 downwards by including some mono-olefin (usually some ethylene) in the monomers. This will improve scrub-resistance.

The simplest way to produce a modified binder polymer is to add plant gum to the polymerisation reaction mixture from which the binder polymer is
20 formed. Preferably the plant gum is obtainable from plant fibre, more

preferably from corn fibre and most preferably the plant gum contains proteo-xylan and/or furanose moieties.

A process is also provided for modifying film forming binder polymers
5 which are binder polymers for coating compositions wherein plant gum of the type described above, preferably corn fibre gum, is added to the polymerisation reaction which produces the binder polymer. Such polymerisations are conventionally performed with the aid of free radical or redox initiators. The temperature at which the polymerisation is carried out
10 depends on the boiling point of the carrier liquid used and the radical flux of the initiator selected. Where the modified binder polymer is made as a dispersion of polymer particles in water, the temperature is preferably from 20 to 98°C, more preferably from 30 to 95°C and most preferably from 50 to 90°C.

15

Without wishing to be bound by this, it is suspected that during the polymerisation the constituents of the plant gum such as corn fibre gum are chemically incorporated into the copolymer, for example by abstraction of labile hydrogen from the furanose by the initiators. Preferably from 0.1 to
20 5wt% (and more preferably 2 to 4wt%) of plant gum, more preferably corn fibre gum is added to the polymerisation reaction mixture where the

percentages are based on the total weight of the monomers from which the binder polymer is to be formed.

A coating composition is also provided wherein the composition contains
5 modified binder polymer as herein described. Preferably the coating composition further contains components usually found in paints such as pigments, fillers, extenders, rheological modifiers, dispersants, antifoams, flow aids, crosslinkers and biocides. Preferably the coating composition contains pigment and more preferably the pigment is titanium dioxide. Even
10 more preferably the pigment is rutile titanium dioxide. Preferably the PVC(TiO₂) is from 5 to 35%, more preferably from 10 to 35%, even more preferably from 12 to 30% and most preferably from 17 to 30%. The PVC(total) is preferably from 8 to 75% depending on the gloss or sheen level of the paint.

15

An aqueous dispersion of the modified film-forming binder copolymer is easily converted into a coating composition by mixing it with all the components of the composition except for, preferably any chelate structuring agent. If a strongly structured composition, the chelate is
20 preferably stirred in just before the composition is filled into cans so that the gel structure develops in the can.

The most significant of the other components are opacifying pigments such as rutile or anatase titanium dioxide or voided organic polymer particles. Typical fillers and extenders include chalk, limestone, kaolin and talc.

5 Silica may also be present as a matting agent. Whilst this invention is of most importance in making paints, it is also possible to omit the opacifier to produce a varnish or woodstain.

The coating compositions preferably have a "Rotothinner" (low shear)

10 viscosity of from 0.15 to 3.0 pascal.sec all measured at 25°C using a 5.6cm diameter spindle rotating at 560 rpm. A strongly structured thixotropic composition preferably has a gel strength at 1 week of at least 50g.cm.

The coating composition is preferably solventborne or waterborne.

15 Waterborne compositions are preferred whereby at least 50% by weight of the carrier liquid in the composition is water. Such compositions release less organic solvents into the atmosphere and are also preferred by users as they also have reduced odour.

20 The use of the modified binder polymer in a coating composition improves the opacity of the coating composition. It is not known by which

mechanism this occurs, although and without wishing to be bound by this, it is thought that the opacifying efficiency of pigments such as titanium dioxide, especially rutile is increased by from 10 to 20%. This allows a greater opacity to be achieved or alternatively reduced concentrations of rutile with a consequent improvement in scrub-resistance and cost.

Accordingly, the invention also provides a method for improving the opacity of coating compositions by employing a modified binder polymer as a binder polymer in a coating composition. Preferably the coating composition contains particulate non-film forming material and more preferably it is titanium dioxide, especially in the form of rutile.

The invention will now be illustrated by the following Examples of which Examples A to E are comparative.

15

The paints were tested for opacity and scrub-resistance as follows:

Contrast Ratio

The opacity was measured using the contrast ratio method according to the following procedure. The paint is spread over a Morest chart Number 9 using a K-bar 6 to give a wet paint film of approximately 60 μm . The paint

is allowed to dry over a period of from 2 to 3 hours at a temperature of about 20°C. One half of the Morest chart is coloured black and the other white. A Spectroflash 600 PLUS spectrophotometer is used to measure the reflected light from the dried paint applied over first the black and then the white half of the Morest chart. The amount of measured light reflected on the black half is divided by the amount reflected from the white side and expressed as a percentage contrast ratio. The measurements are repeated three times and averaged.

Scrub Resistance Test:

The wet scrub resistance was assessed as follows: a solid paint coating was prepared using a 400 micron block spreader, allowing it to dry and aging it in an oven at 40°C for 7 days. The aged paint was tested according to British Standard 7719 of 1994 and a weight loss reported. A weight loss of less than 2mg of paint per cm² is acceptable (pass).

15

The ingredients used in the foregoing examples are listed below and are available from the suppliers or the process indicated.

Acrysol SCT-275 A non-ionic associative thickener available from
Rohm and Haas (UK) Ltd.

20 Aquaflo NHS 300 A polyether thickener available from Hercules.

“Bentone” Ew: Bentonite clay supplied by Rheox Ltd of UK

	China Clay Supreme	China Clay extender available from ECC International, UK
5	Corn Fibre Gum	A plant gum obtained by the process disclosed in US 6,147,206 a summary of which is provided in the description of this specification. The composition, by weight %, of the Corn Fibre Gum obtained by this process is 80% polysaccharide, 5% protein and 15% ash. The polysaccharide component comprised the
10		following components in the proportions indicated; 48.0% xylose, 39.4% arabinose, 8.4% galactose and 4.2% glucuronic acid.
	Gum Arabic	A plant gum obtained from Sigma-Aldrich of Dorset, England. The composition, by weight %, comprising
15		97.9% polysaccharide and 2.1% protein. The polysaccharide component comprised the following components in the proportions indicated; 45.4% galactose, 24.7% arabinose, 13.4% rhamnose and 16.5% glucuronic acid.
20	Araban	A plant gum obtained from British Sugar. The composition, by weight %, comprising 97.1% polysaccharide and 2.9% protein. The polysaccharide

component comprised the following components in the proportions indicated; 42.0% glucose, 8.4% galactose, 10.1% xylose, 35.3% arabinose and 4.2% rhamnose.

- “Dispelair” CF 246: A surfactant supplied by Blackburn Chemicals Ltd of
5 Blackburn, UK
- “Disponil” A1580: A surfactant supplied by Henkel Performance
Chemicals of Germany
- 10 “Blanose” 7L2C: A cellulosic thickener supplied by Hercules Inc of
USA
- “Britomya” V: A calcium carbonate supplied by OMYA UK Ltd of
Surrey, UK
- 15 “Dispex” N40: A surfactant supplied by Allied Colloids of UK
- “Empimin” OT75: A surfactant supplied by Albright & Wilson of UK
- “Fordacal” 30: A calcium carbonate extender supplied by Foramin Co.
Ltd of UK.
- 20 “Lubrizol” 2405: A surfactant supplied by Lubrizol UK LTD of UK
- “Mergal” 711 K6: A biocide supplied by Troy Chemicals Europe BV of
the Netherlands.
- “Microdol” H 200: Dolomite supplied by Omya of Cologne, Germany.
- 25 “Natrosol” 250MR: A cellulosic thickener supplied by Hercules Inc of
USA
- “Perlankrol” ESD60: A surfactant supplied by Akzo Nobel Chemicals Ltd
of the Netherlands
- 30 “Rocima” V189 : A biocide available from Thor Plastics UK, New
Road, Newhaven, UK

“Rhodacal” A246L: A surfactant supplied by Rhodia SA of France

“Ropaque” ULTRA: A voided organic particulate opacifier supplied by
Rohm & Haas of USA

5 Tioxide TR92 Titanium dioxide supplied by Huntsman Chemicals

“Tilcom” AT35: A chelate structuring agent supplied by Tioxide
Specialists Ltd (Huntsman) of Teeside, UK

Example 1**PRODUCTION OF A MODIFIED ACRYLIC BINDER POLYMER:-**

An aqueous dispersion of a binder polymer modified with corn fibre gum was made using the ingredients shown below and according to the

5 procedure described.

	<u>Plant Gum Charge</u>	<u>Weight g</u>
	Water	578.35
	Corn Fibre gum	13.86
10	Sodium bicarbonate	1.32
	Sodium Chloride (pure and vacuum dried)	1.12
	Rhodacal A246 L	<u>1.58</u>
		592.63
15	<u>Seed Monomer Charge</u>	<u>Weight g</u>
	Vinyl acetate	22.85
	Vinyl "Versatate"	4.04
	"Empimin" OT 75	<u>0.28</u>
		27.17
20		
	<u>Seed Initiator Charge</u>	<u>Weight g</u>
	Ammonium persulphate	0.78
	Water	17.07
	Lubrizol 2405	<u>0.54</u>
25		18.39

	<u>Acrylic Monomer Charge</u>	<u>Weight g</u>
	Methyl methacrylate	252.01
	"Disponil" A 1580	20.74
	"Perlankrol" ESD60	3.15
5	2-Ethyl hexyl acrylic	<u>241.58</u>
		517.48
	 <u>Main Initiator Charge</u>	 <u>Weight</u>
10	Ammonium persulphate	0.76
	Water	<u>16.76</u>
		17.52
	 <u>Mop-up initiator charge</u>	 <u>Weight g</u>
15	Ammonium persulphate	0.18
	Water	<u>3.90</u>
		4.08
	 <u>Biocide Solution</u>	 <u>Weight g</u>
20	Rocima V189	1.65
	Water	<u>4.40</u>
		6.05

The plant gum charge was added to a round-bottomed flask fitted with a stirrer and a nitrogen purge. The charge was purged by bubbling nitrogen through it for 5 minutes. The temperature was increased to 75°C and held for 30 minutes. The seed monomer charge was then added to the flask and maintained at 75°C for a further 10 minutes. The seed initiator charge was then added and the temperature increased to 90°C over 30 minutes during

which time an aqueous dispersion of seed copolymer formed, possibly with some bonding of moieties from the plant gum.

The acrylic monomer charge together with the main initiator charge were added dropwise over a period of two hours to the seed copolymer whilst the
5 temperature was maintained at 90°C. During this time, an aqueous dispersion of seeded copolymer of methyl methacrylate and 2-ethyl hexyl acrylate formed with bonding of moieties from the plant gum. On completion of the addition of the acrylic monomers, the mop-up initiator charge was added and the temperature maintained at 90°C for a further 30
10 minutes after which the dispersion was allowed to cool to 37°C. The biocide solution was then added.

The dispersion comprised a copolymer of methyl methacrylate/2-ethyl hexyl acrylate/vinyl acetate/vinyl versatate having a solids content of 46.0 wt%.

15

Example A Comparative Unmodified Binder Polymer

An aqueous dispersion of an unmodified binder polymer was made using the ingredients listed below according to the following process.

	<u>Aqueous charge</u>	<u>Weight g</u>
20	Water	499.93
	Blanose 7L2C	3.32
	Disponil A1580	2.58

Sodium bicarbonate	1.01
Sodium Chloride (pure and vacuum dried)	<u>1.22</u>
	517.13

5

The components of the aqueous charge were added to a round bottom reactor whilst stirring. The temperature of the contents was raised to 75°C. During this heating period a monomer feed mixture was prepared in a separate vessel.

10

<u>Monomer feed mixture</u>	<u>Weight g</u>
Methyl methacrylate	302.74
Acrylic acid (glacial)	6.00
Disponil A1580	23.81
15 Perlankrol ESD60	3.61
2-ethyl hexyl acrylate	<u>290.76</u>
	626.92

An amount of 31.35g of this mixture was removed from the vessel and added to the reactor. The temperature of the reactor contents was held at 75°C for a further 10 minutes during which time an initiator solution consisting of 1.87g of ammonium persulphate in 41.16g of water was made. 9.73g of the initiator solution were removed and added to the reactor. After 10 minutes the seed polymer formed and the temperature was raised over 30 minutes to 90°C. The remaining monomer feed mixture of 595.57g was added to the reactor over two hours during which time 28.01g of the

25

initiator solution were also added. At the end of this period the remaining initiator solution of 5.29g was added to the reactor and held at 90°C for a further hour to ensure complete polymerisation of the monomers. A reactor rinse of 15.38g of water was added followed by 6.64g of biocide solution
5 consisting of 1.80g of Rocima V189 in 4.80g of water.

The solids content was 52.5wt%.

EXAMPLE 2, COMPARATIVE EXAMPLE B and EXAMPLE 3

10 Preparation and Testing of Acrylic Matt Paints

Example 2

A mill base was prepared as follows. An initial charge of 187.8g of water was added to a 1 litre disperser container followed by 20.2g of Orotan 731 and 1.5g Dispelair CF246. The mixture was stirred for 5-6 minutes at about
15 1000rpm using a high speed disperser fitted with a 7cm Cowles blade.
121.2g of Microdol H200, 101.3g of China Clay Supreme and 131.4g of Tioxide TR92 were weighed into a separate container and then added to the 1 litre container. A further 131.4g of Tioxide TR92 was added to the disperser container. The disperser speed was gradually increased to
20 2000rpm and maintained at this speed for a further 5 to 10 minutes during which the pigment and extender started to disperse. A further 70.8g of water

was added followed by 1.5g of Natrosol Plus Grade, the latter added carefully to the top of the vortex formed in the millbase through stirring. As dispersion proceeded the viscosity of the millbase rose and the speed of the disperser was raised to approximately 3000rpm in order to maintain good
5 circulation of the millbase as evidenced by a vortex extending to about halfway into the mixture following the addition of the Natrosol Plus Grade the millbase was dispersed for a total of 25 minutes after which 0.2g of Rocima V189 was added.

10 Paint make-up

To 729.0g of the millbase was added 3.8g of water and stirred at about 600rpm using a paddle stirrer. Whilst stirring the diluted millbase, 220.9g of the aqueous dispersion of modified binder polymer made according to Example 1 was also added followed by 0.4g of ammonia solution finally the
15 stirrer speed was raised to 900rpm and the thickeners were added, comprising 11.5g of Acrysol SCT-275 and 4.8g of Aquaflo NHS300. The resulting paint was stirred for approximately 5 to 10 minutes following the thickener addition and allowed to stand for 16 hours at room temperature.

20 The liquid paint composition was substantially free of coalescing solvents.

The PVC (total) was 58.2% and the PVC (TiO₂) was 25.8%. The contrast ratio was measured at 98.1%.

The dried solid paint was tested for scrub resistance according to British
5 Standard 7719 of 1994 and lost 0.77 mg of paint per cm² (pass).

Comparative Example B

A millbase was made according to Example 2 except that 28.3g of the initial charge of water were replaced by a solvent mixture consisting of 8.1g of
10 benzyl alcohol and 20.2 of Texanol.

To 729.0g of millbase was added 10.9g of water and stirred at about 600rpm using a paddle stirrer. 192.7g of the aqueous dispersion made according to Comparative Resin Example A was added whilst stirring. The remaining additions and conditions were identical to those of Example 2.
15

The liquid paint composition contained 3% by weight of coalescing solvents. The PVC (total) was 58.2% and the PVC (TiO₂) was 25.8%. The contrast ratio was 94.1%.

20 The dried solid paint was tested for scrub resistance according to British Standard 7719 of 1994 and lost 0.76 mg of paint per cm²(pass).

Example 3

A paint was made using the ingredients and according to the method of Example 2 except that the amount of Tioxide TR92 pigment was reduced to
5 achieve a PVC (total) of 55.2% and a PVC (TiO₂) of 20.9%. The contrast ratio was measured to be 94.5%. This is comparable to the contrast ratio of Comparative Example B that used significantly higher PVC (TiO₂) at 25.8% demonstrating more efficient utilisation of the titanium dioxide pigment.

10 The dried solid paint was tested for scrub resistance according to British Standard 7719 of 1994 and lost 0.74 mg of paint per cm² (pass).

Example 4

An aqueous dispersion of a binder polymer modified with corn fibre gum
15 was made using the ingredients shown below and according to the procedure of Example 1. This binder polymer differs from Example 1 in that the seed is based on acrylic monomers.

	<u>Plant Gum Charge</u>	<u>Weight g</u>
20	Water	522.03
	Corn Fibre gum	12.13
	Sodium bicarbonate	1.23

	Sodium Chloride (pure and vacuum dried)	1.05
	Rhodacal A246 L	<u>1.07</u>
		537.51
5	<u>Seed Monomer Charge</u>	<u>Weight g</u>
	Methyl methacrylate	12.91
	2-ethyl hexyl acrylate	12.37
		25.28
10	<u>Seed Initiator Charge</u>	<u>Weight g</u>
	Ammonium persulphate	0.73
	Water	<u>15.90</u>
		16.63
15	<u>Acrylic Monomer Charge</u>	<u>Weight g</u>
	Acetic acid	4.30
	Methyl methacrylate	234.61
	"Disponil" A 1580	19.31
20	"Perlankrol" ESD60	2.93
	2-Ethyl hexyl acrylic	<u>224.89</u>
		486.04
25	<u>Main Initiator Charge</u>	<u>Weight g</u>
	Ammonium persulphate	0.71
	Water	<u>15.59</u>
		16.30
30	<u>Mop-up initiator charge</u>	<u>Weight g</u>
	Ammonium Persulphate	0.16
	Water	<u>16.76</u>
		16.92

	<u>Biocide Solution</u>	<u>Weight g</u>
	Rocima V189	1.54
	Water	<u>4.09</u>
5		5.63

The solids content of the aqueous dispersion was 45.6wt%.

Example 5

- 10 A paint was made was made using the ingredients and process of Example 2 other than the modified binder polymer of Example 4 replaced that of Example 1, on a solids weight for weight basis, and PVC(Total) and PVC(TiO₂) of Example 5 are slightly higher than Example 2, as indicated below.
- 15 The liquid paint composition was substantially free of coalescing solvents. The PVC (total) was 60.5% and the PVC (TiO₂) was 27.4%. The contrast ratio was 95.9%.

The dried solid paint was tested for scrub resistance according to British
20 Standard 7719 of 1994 and lost 1.72 mg of paint per cm² (pass)

Comparative Example C

A paint was made was made using Comparative Unmodified Resin Example A. All other ingredients and amounts were the same as for Example B other than the PVC(Total) and PVC(TiO₂) of Example C are slightly higher than Example B, as indicated below.

- 5 The liquid paint composition contained 3% of coalescing solvents.

The PVC (total) was 60.2% and the PVC (TiO₂) was 27.2%. The contrast ratio was 91.7%.

The dried solid paint was tested for scrub resistance according to British

- 10 Standard 7719 of 1994 and lost 0.72mg of paint per cm² (pass)

Example 6

An aqueous dispersion of a binder polymer modified with gum arabic was made using the ingredients shown below and according to the procedure

- 15 described in Example 1.

	<u>Plant Gum Charge</u>	<u>Weight g</u>
	Water	669.35
	Gum Arabic	12.13
20	Sodium bicarbonate	1.23
	Sodium Chloride (pure and vacuum dried)	1.05
	Rhodacal A246 L	<u>1.07</u>
		683.60

	<u>Seed Monomer Charge</u>	<u>Weight g</u>
	Vinyl acetate	25.03
	Empimin OT 75	<u>0.25</u>
5		25.28
	<u>Seed Initiator Charge</u>	<u>Weight g</u>
	Ammonium persulphate	0.73
	Water	<u>15.90</u>
10		16.63
	<u>Acrylic Monomer Charge</u>	<u>Weight g</u>
	Methyl methacrylate	234.61
	"Disponil" A 1580	19.31
15	"Perlankrol" ESD60	2.93
	2-Ethyl hexyl acrylic	<u>224.89</u>
		481.74
	<u>Main Initiator Charge</u>	<u>Weight</u>
	Ammonium persulphate	0.87
	Water	19.23
25		20.10
	<u>Reactor rinse</u>	<u>Weight g</u>
	<u>(replaces Mop-up initiator charge)</u>	
	Water	13.12
30		
	<u>Biocide Solution</u>	<u>Weight g</u>
	Rocima V189	1.54

Water	<u>4.09</u>
	5.63

The solids content of the aqueous dispersion was 42.9wt%.

5 **Example 7**

A paint was made using the ingredients and process of Example 2 other than the modified binder polymer of Example 6 replaced that of Example 1, on a solids weight for weight basis, and the PVC(Total) and PVC(TiO₂) of Example 7 are slightly higher than Example 2, as indicated below.

- 10 The liquid paint composition was substantially free of coalescing solvents. The PVC (total) was 59.6% and the PVC (TiO₂) was 26.4%. The contrast ratio was 96.3%.

The dried solid paint was tested for scrub resistance according to British

- 15 Standard 7719 of 1994 and lost 1.78mg/cm² (pass)

Example 8

An aqueous dispersion of a binder polymer modified with Araban was made using the same procedure and ingredients as in Example 6 except that the

- 20 Plant Gum Charge contained 605.55g of water, 24.24g of Araban, 1.07g of Rhodocol A246L and 1.05g Pure vac dried sodium chloride. The solids content of the dispersion was 44.2wt%.

Example 9

A paint was made using the ingredients and process of Example 2 other than the modified binder polymer of Example 8 replaced that of Example 1,
5 on a solids weight for weight basis.

The liquid paint composition contained 0.8% coalescing solvents.

The PVC (total) was 59.0% and the PVC (TiO₂) was 26.7%. The contrast ratio was 95.8%. The dried solid paint was tested for scrub resistance
10 according to British Standard 7719 of 1994 and lost 1.38mg of paint per cm² (pass)

CLAIMS

1. A film-forming binder polymer for a coating composition wherein the polymer is modified by the presence of bonded moieties obtainable
5 from plant gum.
2. A binder polymer according to Claim 1 wherein the plant gum is obtainable from plant fibre.
3. A binder polymer according to Claim 1 or Claim 2 wherein the plant gum is obtainable from corn fibre.
- 10 4. A binder polymer according to any one of the preceding Claims wherein the bonded moieties comprise proteo-xylans.
5. A binder polymer according to any one of the preceding Claims wherein the bonded moieties comprise furanose.
6. A binder polymer according to any one of the preceding Claims
15 wherein the bonded moieties are chemically attached to the binder polymer.
7. A binder polymer according to any one of the preceding Claims wherein the plant gum comprises a mixture of polysaccharide and protein.

8. A binder polymer as claimed in Claim 1 wherein the bonded moieties are derived by adding plant gum to the polymerisation reaction mixture from which the binder polymer is formed.
9. A binder polymer as claimed in Claim 8 wherein the plant gum is
5 corn fibre gum.
10. A binder polymer according to any one of the preceding claims wherein the polymer is an aqueous dispersion of particles.
11. A process for modifying film-forming binder polymers which are binder polymers for coating compositions wherein plant gum is added
10 to the polymerisation reaction which produces the binder polymer.
12. A process as claimed in Claim 11 wherein the plant gum is corn fibre gum.
13. A coating composition wherein the composition contains a modified binder polymer as claimed in any one of the preceding claims.
- 15 14. A coating composition according to Claim 13 wherein the composition further contains at least one component selected from the group consisting of pigments, fillers, extenders, rheological modifiers, dispersants, antifoams, flow aids, crosslinkers and biocides.
- 20 15. A coating composition according to claim 14 wherein the selected component is pigment.

16. A coating composition according to Claim 15 wherein the pigment is titanium dioxide.
17. A coating composition according to Claim 16 wherein the pigment is rutile.
- 5 18. A coating composition according to any one of Claims 1 to 17 having a PVC(TiO₂) of from 5 to 35%.
19. A method for improving the opacity of coating compositions wherein the method comprises employing a modified binder polymer according to any one of Claims 1 to 10 as a binder in a coating
10 composition.
20. A method for improving the opacity of coating compositions comprising particulate non-film forming materials wherein the method comprises employing a modified binder polymer according to any one of Claims 1 to 10 as a binder.
- 15 21. A method for improving the opacity of coating compositions according to Claim 20 wherein the particulate non-film forming material is titanium dioxide.
22. A method for improving the opacity of coating compositions according to Claim 20 wherein the particulate non-film forming
20 material is rutile.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/005758A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D201/02 C09D151/00 C09D5/16

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	GB 1 039 540 A (REED PAPER GROUP LTD) 17 August 1966 (1966-08-17) abstract; claims 1-21 -----	1-4, 6-16, 18-20,22 17,21
X	EP 0 949 307 A (ICI PLC) 13 October 1999 (1999-10-13) abstract; claims 1-10 page 2, lines 13-16 page 4, lines 33-38 -----	1-3,6, 8-22
X A	US 3 891 580 A (MORRIS HORTON HAROLD ET AL) 24 June 1975 (1975-06-24) abstract; claims 1-16 ----- -/-	1-4, 6-16, 18-21 17,21

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

16 August 2004

Date of mailing of the international search report

24/08/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bergmans, K

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/005758

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 090 195 A (ANDERSEN PER JUST ET AL) 18 July 2000 (2000-07-18) abstract; claims 1-48 -----	1-4,6-12
X	US 5 439 964 A (OHST HOLGER ET AL) 8 August 1995 (1995-08-08) abstract; claim 1 column 5, line 20 -----	1-3,5,6, 8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/005758

Patent document cited in search report		Publication date	Patent family member(s)	Publication date			
GB 1039540	A	17-08-1966.	CH 435966 A	15-05-1967			
			DE 1571138 A1	26-11-1970			
			FR 1439865 A	27-05-1966			
			NL 6413670 A	26-05-1965			
			SE 307067 B	16-12-1968			
EP 0949307	A	13-10-1999	AT 206739 T	15-10-2001			
			AU 751224 B2	08-08-2002			
			AU 3148199 A	01-11-1999			
			BR 9909475 A	19-12-2000			
			CA 2326780 A1	21-10-1999			
			DE 69900338 D1	15-11-2001			
			DE 69900338 T2	16-05-2002			
			WO 9952985 A1	21-10-1999			
			EP 0949307 A1	13-10-1999			
			US 2002128380 A1	12-09-2002			
			US 6384132 B1	07-05-2002			
			US 3891580	A	24-06-1975	US 3804653 A	16-04-1974
			US 6090195	A	18-07-2000	US 5830305 A	03-11-1998
US 5385764 A	31-01-1995						
US 5766525 A	16-06-1998						
US 5676905 A	14-10-1997						
US 5508072 A	16-04-1996						
US 6030673 A	29-02-2000						
US 5660900 A	26-08-1997						
US 5783126 A	21-07-1998						
US 5662731 A	02-09-1997						
US 5683772 A	04-11-1997						
US 5709827 A	20-01-1998						
US 5679145 A	21-10-1997						
US 5618341 A	08-04-1997						
US 5658603 A	19-08-1997						
US 5705239 A	06-01-1998						
US 5830548 A	03-11-1998						
US 5868824 A	09-02-1999						
AT 223297 T	15-09-2002						
AU 677231 B2	17-04-1997						
AU 4995893 A	15-03-1994						
AU 706484 B2	17-06-1999						
AU 5280398 A	02-04-1998						
AU 683249 B2	06-11-1997						
AU 6354494 A	14-09-1994						
BR 9306895 A	08-12-1998						
BR 9405730 A	28-11-1995						
CA 2137347 A1	03-03-1994						
CA 2156050 A1	01-09-1994						
CN 1403349 A	19-03-2003						
CN 1099711 A	08-03-1995						
CN 1250736 A	19-04-2000						
DE 69431293 D1	10-10-2002						
DE 69431293 T2	30-04-2003						
EG 20545 A	31-07-1999						
EG 20546 A	31-07-1999						
EP 1155794 A2	21-11-2001						
EP 0662029 A1	12-07-1995						
EP 0686082 A1	13-12-1995						

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP2004/005758

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 6090195	A	IL 107722 A	22-02-1998	
		IL 108671 A	16-08-1998	
		JP 8500075 T	09-01-1996	
		JP 8507035 T	30-07-1996	
		NZ 255666 A	24-04-1997	
		NZ 263022 A	24-11-1997	
		NZ 314299 A	26-08-1998	
		RU 2143341 C1	27-12-1999	
		WO 9404330 A1	03-03-1994	
		WO 9419172 A1	01-09-1994	
		US 5626954 A	06-05-1997	
		US 5543186 A	06-08-1996	
US 5439964	A	08-08-1995	DE 4227419 A1	24-02-1994
		DE 59304179 D1	21-11-1996	
		EP 0584613 A1	02-03-1994	
		JP 6207084 A	26-07-1994	