

**(METH)ACRYLIC COMB POLYMERS HAVING A HYDROXY
POLYALKYLENE GLYCOL FUNCTION, USE THEREOF AS A SHEAR RATE
THINNING AGENT IN COATING SLIPS AND SLIPS CONTAINING SAME**

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The present invention concerns the field of paper and focuses more particularly on certain additives known by the expression "rheology modifiers". These are used in the formulation of coating dispersions which are aqueous formulations designed to be applied to the surface of the sheet of paper.

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It is based on a technology now inscribed in the state of the art: that of comb polymers featuring a (meth) acrylic skeleton with side chains of the hydroxy or alkoxy polyalkylene glycol type, and which enter into the composition of paper coating dispersions. It offers an improvement based on the particular choice of a hydroxy group at the end of the side

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chain.

Compared to their predecessors of the prior art, the comb polymers of the present invention lead to a maintenance of water retention and viscosity at low shear gradient, but very significantly decrease the viscosity under high stress. This latter property, which

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reveals the polymers of the invention as shear-thinning agents, is particularly interesting for counteracting the phenomenon of increased blade pressure. This allows elevated dry extract and/or high speed deposit coating which corresponds to the current needs of the paper manufacturer.

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In the manufacture of the paper sheet by coating, there is deposited on the surface of the base paper an aqueous composition called a "coating dispersion" the function of which is to confer on the said sheet a number of properties such as opacity, brightness, whiteness or again, printability by gravure or offset printing processes.

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These coating dispersions consist of water, one or more mineral fillers such as natural or synthetic calcium carbonate, kaolin, talc, or again, titanium oxide, one or more binders of a natural origin (like the carbohydrates such as starch, casein, carboxymethylcellulose - CMC), or of a synthetic origin (such as the styrene-butadiene, styrene-acrylic, vinyl

copolymer latexes), as well as various additives (dispersants, water retention agents, optical brighteners, etc.).

Among these additives, there is a special category that allows the optimization of the rheological characteristics of the dispersion in relation to the coating process parameters and the properties sought for the said dispersion: those of rheology modifiers. As indicated by their name, these products have the function of controlling the rheology of the dispersion, i.e. of adjusting its viscosity as a function of the stress that is applied to it.

In this regard, it is in the first place important to have an easily pumpable and filterable dispersion in the feed circuits of the coating process, with no tendency for the formation of foam or coating splash as well as a too rapid sedimentation. This requirement corresponds to an increase in the viscosity under low gradient shear, or a Brookfield TM viscosity measured at 100 RPM and at 25°C with the device of the same name, without which the dispersion is too liquid.

Another important rheological characteristic is the viscosity under high shear gradient, as expressed by an ACAV viscosity at 25°C, measured in a capillary viscometer where the dispersion can be subjected to high shear gradients (from 10^5 to $3 \times 10^6 \text{ s}^{-1}$) of the same order of magnitude as those observed during the coating process in the application of the coating blade scraping off the excess dispersion deposited. The viscosity under high shear gradient is a determinant of the blade pressure to be applied. The higher the viscosity under high shear gradient, the higher the blade pressure must be to control the weight of the coat deposited.

However, the increase in the dry extract of coating dispersions and the increase in coating rates are trends that have been observed in recent years, because they have economic and/or quality advantages. Indeed, an increase in the dry extract of the coating dispersion permits a reduction in costs: the amount of energy needed for drying the dispersion is thus decreased. This increase also allows an improvement in the quality of the paper: the penetration of the dispersion into the base paper is reduced, which is favourable in the development of brightness. But this increase in dry extract leads to an increase in the viscosity under shear and as a consequence, to an increase the blade pressures required.

Higher coating speeds generate an increase in the hydraulic force on the blade and thus in the pressure to be exerted. Increases in blade pressure may then reach unacceptable levels and ones that are usually accompanied by dispersion overflows known by the terms "foams" or "beads".

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It is therefore useful for the person skilled in the art to have a rheology modifier in order to obtain the necessary low shear gradient viscosity and to reduce the viscosity under high gradient in order to exploit the benefits of an increase in speed or an increase in the dry extract in coating dispersions without exceeding the limits of his process and avoiding the formation of overflows. This problem is reported in document WO 84 / 04491. This double problem of increasing the Brookfield TM viscosity and reducing the ACAV viscosity can be summarized as a search for a so-called "shear-thinning" agent.

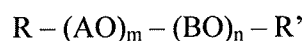
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In parallel with these rheological aspects is another fundamental property of the coating dispersion: its water retention: After deposit on the base paper, the dispersion has a natural tendency to transfer part or all of the water-soluble substances it contains into base paper. An attempt is therefore made to reduce as much as possible the migration of water and water-soluble substances in order to prevent an evolution of the rheology of the unused coating dispersion that is recycled in the coating process. This is referred to as the phenomenon of water retention which one seeks to improve, i.e. to increase.

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A special category of rheology modifiers has been known about for decades, one which allows an increase in the Brookfield TM viscosity of coating dispersions while improving their water retention. These are the comb polymers with a (meth) acrylic skeleton with alkoxy polyalkylene glycol side chains with the following general formula:

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where:

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- m and n are integers that are less than or equal to 150, with at least one being a non-zero.
- A and B designate alkyl groups that differ from one another and have 2 to 4 carbon atoms, group AO preferentially designating ethylene oxide and group BO preferentially designating propylene oxide.

- R designates a polymerizable unsaturated function,
- R' designates a hydroxy or alkyl group with 1 to 5 carbon atoms.

These structures are amply described in documents WO 01/96007 A1, WO 04 / 044022 A1, WO 04 / 041883 A1, WO 07 / 069037 A1 and WO 08 / 149226 A1. These polymers can be introduced in the coating dispersion through the suspension of mineral substances in which they improve the rheology (WO 01/96007 A1). In addition to their ability to increase the Brookfield TM viscosity of the dispersion, they help to improve the optical azuration (WO 04 / 044022 A1) and brightness (WO 04 / 041883 A1) thereof. They are also known to increase the water retention of the dispersion (WO 07 / 069037 A1). However, it is also known that they increase very significantly the viscosity under high shear gradient (WO 08 / 149226 A1) which is not compatible with a high speed and/or elevated dry extract coating.

In addition, these polymers appear as complex structures, in the sense that they are defined through multiple variables: the anionic species for the monomer forming the main chain, the possibility of implementing a termonomer and/or a cross-linking agent, and for the side chain, the nature of the polymerizable function R, the nature and number of alkyloxy units, and finally, the identity of the terminal group (hydroxy or alkoxy with 1 to 5 carbon atoms). In addition, the polymers predominantly illustrated in the above documents are acrylic acid and methacrylic acid copolymers, with methoxy polyethylene glycol methacrylate.

Now in an unexpected and quite advantageous manner, the Applicant has demonstrated that the move to side chains terminated by hydroxy groups leads to structures that are both new and that enable the maintenance of water retention and Brookfield TM viscosity at levels comparable to those achieved with comb polymers of the prior art with alkoxy terminals, but with an extremely marked reduction in the ACAV viscosity. Nobody had even thought of making such a substitution at the level of the terminal group of the side chain, and no factor could enable a predication that this choice would lead to such a benefit in the above-noted coating conditions.

In terms of results, and with respect to similar comb polymers but ones with the side chains terminated by an alkoxy group according to the prior art, the polymers of the present invention behave like:

- water retention agents that are at least equivalent,
- 5 - agents capable of increasing the viscosity under low shear gradient, at a comparable level,
- shear-thinning agents, in the sense that they considerably decrease viscosity under high shear gradient.

There are henceforth available rheological additives that are perfectly suited for use in a
10 coating dispersion with an elevated dry extract and/or intended to be applied at high speed to the sheet of paper.

It is important to indicate that the substitution of the terminal alkoxy group by a hydroxy group on the side chain is made possible by a very specific technology enabling the
15 manufacture of such macromonomers that are then copolymerized with (meth) acrylic monomers. This technology is the subject of US patent 6 034 208 B1. It is important to note that the technical domain relative to this patent is that of concrete and cement: the merit of the Applicant is all the greater, since she was able to identify a technical solution in a sector that is very remote from her own. Finally, it should be noted that the comb
20 polymers that are the subject of this latter patent have a mean molar mass by weight between 5,000 g/mol and 100,000 g/mol, which is a notable point of distinction with the polymers of the present invention in which the mean molar mass by weight is at least equal to 1,000,000 g/mol.

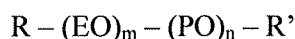
25 Also, a first object of the present invention consists of the above-mentioned polymers. Indeed, these latter are new compared to the structures described in patents WO 01/96007 A1, WO 04 / 044022 A1, WO 04 / 041883 A1, WO 07 / 069037 A1 and WO 08 / 149226 A1, to the extent that their definition results from multiple choices from the many lists which previously defined in a generic manner the comb polymers of the prior art. They
30 are also new with respect to the structures described in US patent 6 034 208 B1, as a result of their much higher mean molar mass by weight.

A second object of the present invention lies in the aqueous solution consisting of water and these polymers. A third object consists in the use of these polymers as agents having

the function of shear-thinning a coating dispersion. A fourth object resides in the coating dispersion that contains these polymers, and a final object is in a coating process for a sheet of paper that employs such a dispersion.

5 The first object of the present invention is a comb polymer characterized in that it consists of, expressed in the molar percentage of each of its constituents:

- a) from 60% to 90% acrylic and/or methacrylic acid, and preferentially acrylic acid and methacrylic acid,
- 10 b) from 10% to 40% of a monomer with the formula:



where:

- 15 - m and n are non-zero integers less or equal to 150,
- EO and PO respectively designate ethylene oxide and propylene oxide,
- R designates the methacrylate function,
- R' designates a hydroxy group.

20 In a variant that is preferred and indicated above, the monomer a) is a mixture of acrylic acid and methacrylic acid. It is demonstrated that it is according to this variant that the greatest decrease in viscosity under high shear gradient is obtained.

This polymer is also characterized in that it presents a mean molar mass by weight of
25 between 1,000,000 and 6,000,000 g/mol, as determined by GPC. Reference can be made to the measurement technique described in document WO 07 / 069037 A1.

The said polymer is obtained by the known methods of conventional free radical copolymerization in solution, in direct or inverse emulsion, in suspension or precipitation
30 in suitable solvents, in the presence of known catalytic systems and transfer agents, or by processes of controlled radical polymerization such as the method known as Reversible Addition Fragmentation Transfer (RAFT), the method known as Atom Transfer Radical Polymerization (ATRP), the method called Nitroxide Mediated Polymerization (NMP), or even the method referred to as Cobaloxime Mediated Free Radical Polymerization.

It is obtained in the acid and possibly distilled form. It can also be partially or totally neutralized by one or more neutralization agents preferentially selected from the hydroxides of sodium and potassium and their mixtures.

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Another object of the present invention consists of an aqueous solution characterized in that it contains water and the above-mentioned comb polymer.

This solution is characterized in that it presents a dry extract of between 10% and 45% by dry weight of the said comb polymer in relation to its total weight.

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In addition, the aqueous solution of polymer can contain another rheological additive, which is preferentially an emulsion of the ASE type (inflatable alkali emulsion) constituted of (meth) acrylic acid and an ester of this (meth) acrylic acid chosen from ethyl and/or butyl acrylate, or an emulsion of the HASE (hydrophobically modified alkali soluble emulsion) type. The manufacturing method for these mixtures is described in document WO 08 / 149226 A1.

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A third object of the present invention is the use of the aforementioned comb polymer in a paper coating dispersion as a shear-thinning agent of the said dispersion. As already explained, the shear-thinning character here means that the said polymer enables a reduction of the viscosity under high shear gradient (ACAV viscosity), with respect to the same comb polymer of the prior art, but not having a terminal hydroxy group on its side chain.

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Another object of the present invention is a coating dispersion containing the aforementioned comb polymer.

This dispersion is also characterized in that it contains:

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- (a) from 3 parts to 20 parts, preferentially from 5 parts to 15 parts by dry weight of binder per 100 parts by dry weight of mineral substances.
- (b) from 0.1 parts to 2 parts, preferentially from 0.1 parts to 1.5 parts by dry weight of comb polymer per 100 parts by dry weight of mineral substances.
- (c) water in a quantity by weight of between 20% and 80%, in relation to the total weight of the coating dispersion.

10 The Applicant indicates that the person skilled in the art can then add other additives used in the usual composition of a coating dispersion, such as biocides, anti-foam agents, optical brighteners and optical brightener media, without however this list being exhaustive.

15 The dispersion is also characterized in that the mineral substance is selected from natural or synthetic calcium carbonate, kaolin, talc and mixtures of these substances.

It is also characterized in that the binder is chosen from among the water-soluble binders and notably starch, or from among the synthetic latex polymer binders such as styrene-acrylic and styrene-butadiene or their mixtures, or mixtures of these binders.

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Finally, in a particular variant corresponding to a so-called "high dry extract" dispersion, it is also characterized in that it contains 20% to 35% by weight of water.

25 A last object of the present invention consists of a process for coating a sheet of paper by the application of the aforementioned dispersion to the surface of the said sheet.

The following examples will allow a better understanding of the present invention, without however limiting its scope.

EXAMPLES

This test illustrates the manufacture of 3 paper coating dispersions, each of them using an aqueous emulsion at 25% by dry weight of a comb polymer according to the prior art (test
5 No. 1), or a comb polymer according to the invention (tests No. 2 and 3).

For each of these tests, a coating dispersion is prepared consisting of:

- 100 parts by dry weight of calcium carbonate marketed by the company OMYA™ under the name Hydrocarb™ 95 ME,
- 10 - 0.6 part by dry weight (in relation to the dry weight of calcium carbonate) of the polymer to be tested,
- 8 parts by dry weight of a styrene-butadiene latex marketed by the DOW™ CHEMICALS company under the name DL 966,
- 0.4 part by dry weight of polyvinyl alcohol marketed by the CLARIANT™ company
15 under the name Mowiol™ 4-98,
- 0.5 part by dry weight of an optical brightener marketed by the LANXESS™ company under the name Blankophor™ P,

The dry extract of the dispersion is set at 70.5% of its total weight.
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Test No. 1 illustrates the prior art and uses a polymer consisting of 67.5% in moles of acrylic acid, 17.5% in moles of methacrylic acid and 15% in moles of a monomer of formula (I) in which $m = 44$, $n = 0$ and R' is the methyl group.

Test no. 2 illustrates the preferred variant of the invention in which the carboxylic acid
25 monomer is a mixture of acrylic and methacrylic acid, and which implements a polymer formed from 67.5% in moles of acrylic acid, 17.5% in moles of methacrylic acid and 15% in moles of a monomer of formula (I) in which $m = 30$, $n = 70$ and R' is the hydroxy group.

Test no. 3 illustrates the invention, and implements a polymer made up of 85% in moles
30 of acrylic acid and 15% in moles of a monomer of formula (I) in which $m = 30$, $n = 70$ and R' is the hydroxy group.

These 3 polymers have a mean molar mass by weight in the order of 3,000,000 g/mol.

The Brookfield™ viscosities (μ_B) and ACAV viscosities (μ_{ACAV}) (measured at a shear gradient of 10^6 s^{-1}) are determined at 25°C as well as the water retention (r_{H_2O}). Reference can be made to documents WO 07 / 069037 A1 and WO 08 / 149226 A1 for their determination and the apparatus used.

The results obtained are listed in table 1.

Test No.	Prior Art Invention	μ_B (mPa.s)	μ_{ACAV} (mPa.s)	r_{H_2O}
1	Prior Art	780	171	114
2	Invention	980	101	112
3	Invention	850	158	112

Table 1

These results demonstrate that while maintaining the Brookfield™ viscosity and the water retention at a level equivalent to the prior art, the polymers of the present invention enable a very large reduction in viscosity under high shear gradient.

This advantage is decisive in offsetting the blade pressure increase, particularly if it is desired to deposit this dispersion on a sheet of paper at high speed.

In addition, the best results are obtained for the polymer according test No. 2, which corresponds to the preferred variant of the invention implementing a mixture of acrylic and methacrylic acids.

Test n° 4 illustrates the prior art and uses a polymer consisting 70% by mole of acrylic acid, 15% by mole of methacrylic acid and 15% by mole of a monomer of formula (I) in which $m=44$, $n=0$ and R' is the methyl group.

Test n° 5 illustrates the prior art and uses a polymer consisting 85% by mole of methacrylic acid, 15% by mole of a monomer of formula (I) in which $m=44$, $n=0$ and R' is the methyl group.

5 Test n° 6 illustrates the prior art and uses a polymer consisting 85% by mole of methacrylic acid, 15% by mole of a monomer of formula (I) in which $m=110$, $n=0$ and R' is the methyl group.

10 Test n° 7 illustrates the preferred variant of the invention in which the carboxylic monomer is a blend of acrylic and methacrylic acids, and uses a polymer consisting 70% by mole of acrylic acid, 15% by mole of methacrylic acid and 15% by mole of a monomer of formula (I) in which $m=15$, $n=46$ and R' is the hydroxy group.

Test n° 8 illustrates the invention and uses a polymer consisting 85% by mole of acrylic acid, 15% by mole of a monomer of formula (I) in which $m=15$, $n=46$ and R' is the hydroxy group.

These 5 polymers have an average molar mass by weight of the order of 2,500,000 g/mol.

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The Brookfield™ (μ_B) and ACAV (μ_{ACAV}) viscosities (measured at a shearing gradient of 10^6 s^{-1}) are determined at 25 °C as is the water retention (r_{H_2O}). Reference may be made to the documents WO 07/069037 A1 and WO 08/149226 A1 for their determination and the apparatus used.

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The results obtained are shown in table 2.

Test n°	Prior Art Invention	μ_B (mPa.s)	μ_{ACAV} (mPa.s)	r_{H_2O}
4	Prior art	800	170	112
5	Prior art	750	165	108
6	Prior art	820	171	108
7	Invention	1020	102	110
8	Invention	1000	160	110

Table 2

The same conclusions are reached as for table 1.

5 Lastly, we add that in tests n° 1 to 8 the polymers were introduced into the coating in the form of an aqueous solution of a dry polymer extract equal to 30% by weight of the total weight of the said solution.

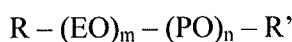
CLAIMS

1 – Comb polymer characterized in that it consists of, expressed as molar percentages of each of its constituents:

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- a) 60% to 90% acrylic and/or methacrylic acid, and preferentially acrylic acid and methacrylic acid,
- b) 10% to 40% of a monomer with the formula:

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where:

- m and n are non-zero integers less or equal to 150,
- EO and PO respectively designate ethylene oxide and propylene oxide,
- R designates the methacrylate function,
- 15 - R' designates a hydroxy group.

2 - Polymer according to claim 1 characterized in that it presents a mean molar mass by weight of between 1,000,000 and 6,000,000 g/mol, as determined by GPC.

20 3 - Aqueous solution characterized in that it contains water and the comb polymer according to one of the claims 1 or 2.

4 - Solution according to claim 3 characterized in that it presents a dry extract of between 10% and 45% by dry weight of the said comb polymer in relation to its total weight.

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5 - Solution according to claim 4 characterised in that it contains another rheological additive which is preferentially an emulsion of the ASE type (inflatable alkali emulsion) constituted of (meth) acrylic acid and an ester of this (meth) acrylic acid chosen from ethyl and/or butyl acrylate, or an emulsion of the HASE (hydrophobically modified alkali
30 soluble emulsion) type.

6 - Use, in a paper coating dispersion as a shear-thinning agent of the said dispersion, of the comb polymer according to one of claims 1 or 2.

7 - Coating dispersion containing the comb polymer according to one of claims 1 or 2.

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8 - Dispersion according to claim 7 characterized in that it contains:

(a) from 3 parts to 20 parts, preferentially from 5 parts to 15 parts by dry weight of binder per 100 parts by dry weight of mineral substances.

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(b) from 0.1 parts to 2 parts, preferentially from 0.1 parts to 1.5 parts by dry weight of comb polymer per 100 parts by dry weight of mineral substances.

(c) water in a quantity by weight of between 20% and 80%, in relation to the total weight of the coating dispersion.

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9 - Dispersion according to one of claims 7 or 8 characterized in that it contains other additives chosen from among biocides, anti foam agents, optical brighteners and optical brightener media.

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10 - Dispersion according to one of claims 7 to 9 characterized in that the mineral substance is selected from natural or synthetic calcium carbonate, kaolin, talc and mixtures of these substances.

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11 - Dispersion according to claims 7 to 10 characterized in that the binder is chosen from among the water-soluble binders and notably starch, or from among the synthetic latex polymer binders such as styrene-acrylic and styrene-butadiene or their mixtures, or mixtures of these binders.

12 - Dispersion according to one of claims 7 to 11 characterized in that it contains 20% to 35% by weight of water.

5 13 - Coating process for a sheet of paper by application to the surface of the said sheet the dispersion according to one of claims 7 to 12.