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(54) Title: DISPERSING AGENT

(57) Abstract: The invention relates to a dispersing agent or salt thereof, comprising at least one dendrimer, said dendrimer comprising functional groups, that have reacted with a functional moiety, said moiety being defined as R-X, X being a pigment affinic group, and R being a linking moiety chain having at least 2 atoms in the chain, with the proviso that the functional group and the pigment affinic group are different.



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Dispersing agent

The present invention relates to a dispersing agent or salt thereof, based on a compound containing at least one pigment affinic group.

The invention further relates to the use of said dispersing agents, powdered or fibrous solid substances (fillers, pigments and the like), to be
5 included in liquid systems, which are coated with such dispersing agents.

To introduce solid substances, such as pigments, into liquid media, high mechanical forces are necessary. This depends to a large extent on the solid substance's wettability by the surrounding medium, as well as on the affinity for this medium. In order to reduce these dispersing forces, it is
10 conventional to use dispersing agents which facilitate incorporating the substances. This mostly concerns surface-active agents or surfactants, of anionic or cationic or non-ionic structure. In relatively low amounts of addition, these agents are either applied directly to the solid substance or added to the dispersing medium. Through such a surfactant, the energy
15 required for the dispersion is considerably reduced.

Further, it is known that such solid substances, after dispersion, tend to reaggregate, which nullifies the initially induced dispersing energy and leads to serious problems. This phenomenon can be explained by *inter alia* London/van der Waals' forces, by which the solid substances are mutually
20 attracted. In order to nullify these attractive forces, adsorption layers should be provided on the solid substances. This occurs through the use of such surfactants or polymers.

During and after the dispersion, however, there arises an interaction of the surrounding medium with the solid particle, so that a desorption of the
25 surfactant can arise in exchange for the surrounding medium present in a higher concentration. However, in most cases this surrounding medium is incapable of building up such stable adsorption layers, so that the entire system flocculates. This is evidenced by *inter alia* an increase of the viscosity

in liquid systems, loss of gloss, color shifts in paints and coatings, insufficient development of coloring power in pigmented plastics and lacquers, as well as a decrease of the mechanical strength in reinforced plastics.

In European patent applications 154.678, 438.836 and 520.586
5 dispersants are described, based on the reaction product of a polyisocyanate with a functionality of 2.5 to 6 with a compound containing a ring structure with at least one basic nitrogen atom in the ring.

These known dispersants are typically based on cyclic compounds that are attached to the polyisocyanate via an amino- or hydroxy-functional
10 side chain. Compounds representative thereof are
1-(2-aminoethyl)piperazine, 2-amino-6-methoxybenzothiazole,
4-(2-aminoethyl)pyridine, 4-(aminomethyl)pyridine,
3-amino-1,2,4-triazole, 1-(3-aminopropyl)imidazole,
4-(2-hydroxyethyl)pyridine and 1-(2-hydroxyethyl)imidazole.

15 These known products are useful for a large number of applications. However, a disadvantage, among others, is that the products provide only a limited viscosity reduction of highly filled pigmented dispersions and the build-up of pseudoplastic and thixotropic flow behaviour.

The previously mentioned polymers have molecular weights in the
20 range of 8000 tot 20000 and a distinctive linear structure. Such linear polymers with pending polar/apolar functional groups are also able to interact with themselves by polar force and prevent Newtonian flow. More in particular the known dispersant provide insufficient reduction in viscosity, especially for state of the art automotive paints.

25 In WO-A 9726984 a dispersing agent is described, based on a different kind of active cyclic compound.

It is an object to provide a new range of dispersants, which have advantageous properties, such as flow behaviour that can approach Newtonian flow, having a low yield value, while maintaining good compatibility and steric
30 hindrance build-up to prevent flocculation.

The invention is based on the use of dendrimers (as defined herein) as core material for the dispersing agent. This results in a very specific three dimensional structure with advantageous dispersing properties.

5 The invention is accordingly directed to a dispersing agent or salt thereof, comprising at least one dendrimer, said dendrimer comprising functional groups, that have reacted with a functional moiety, said moiety being defined as -R-X, X being a pigment affinic group, and R being a linking moiety chain having at least 2 atoms in the chain, with the proviso that the
10 functional group and the pigment affinic group are different.

Basically the invention is concerned with a dendrimer having a plurality of functional groups, to a number of which functional groups a linking moiety is attached, the linking group connecting a functional moiety to the dendrimer.

15 The functional groups of the dendrimer are generally selected from those groups that are able to connect to a linking chain, such as hydroxyl, -NCO, carboxyl or amine groups. To these groups it is possible to connect a polyester, polyether or other chain. The linking chain has to have the ability to connect to the functional moiety. The linking chain may be based on
20 dicarboxylic acids, diol, diamines, hydroxycarboxylic acids, hydroxyamines, amino-carboxylic acids, and the like.

Within the scope of the invention, the term dendrimers refers to three-dimensional, highly branched oligomeric or polymeric molecules. The dendrimers used in accordance to the invention comprise a core, a number of
25 branching generations and an external surface composed of functional, reactive groups. A branching generation is composed of structural units that are bound radially to the core or to the structural units of a previous generation and which extend outwards. The structural units have at least two monofunctional groups and/or at least one monofunctional group and one
30 multifunctional group. The term multifunctional is understood as having a

functionality of 2 or higher. To each functionality, a new structural unit may be linked, a higher branching generation being produced as a result. The structural units may either be the same (they are repeated, therefore) for each successive generation, or they may be different. Dendrimers can be

5 characterized, inter alia, on the basis of a degree of branching. The term degree of branching of a dendrimer of a particular generation is understood, here and hereinafter, as the ratio between the number of branchings present and the maximum possible number of branchings in a completely branched dendrimer of the same generation. The term functional end groups of a

10 dendrimer refers to those reactive groups which form part of the external surface. The branchings may occur with greater or lesser regularity. Whilst it is possible, in the dendrimers which can be used within the scope of the invention, for the branchings at the external surface of the dendrimer all to be of the same generation, it is also possible for the branchings at the surface to

15 be of different generations. The latter may be the case, for example, if the synthesis of the dendrimers proceeds in a less controlled manner.

The term dendrimers is also understood, according to the invention, as dendrimers having defects in the branching structure, dendrimers having an incomplete degree of branching, asymmetrically branched dendrimers, star

20 polymers, highly branched polymers, highly branched copolymers and/or block copolymers of highly branched and not highly branched polymers.

In principle, all dendrimers having functional end groups can be considered for use according to the invention. The best results are often achieved either with perfectly branched dendrimers or with highly branched

25 polymers or highly branched copolymers. The term perfectly branched dendrimers refers to those dendrimers in which, in each generation, at least 95%, preferably 99% of the functionality of the functional groups in the structural units has reacted with a functional group of a structural unit of the next generation.

The number of functional end groups of a dendrimer which is provided with a modifying group according to the invention generally varies according to the type and generation of the dendrimer used and the type and dimensions of the modifying group. Preferably, dendrimers are used in which at least 30% of the functional end groups of the dendrimer are provided with a modifying group, more preferably at least 50%, even more preferably at least 70% and most preferably at least 90%. The absolute number of functional groups per dendrimer is at least 8, but preferably it is higher, such as at least 12.

Dendrimers suitable within the scope of the invention are dendrimers based on, for example, a polyester, polyether, polythioether, polyamide, polyetherketone, polyalkylene imine, polyamido amine, polyether amide, polyarylene, polyalkylene, aromatic polyalkylene, polyaryl acetylene and/or a phosphorus-or silicon-containing dendrimer, or a combination thereof. Preferably, use is made of a dendrimer based on a highly branched polyester, for example a polyester prepared from 2,2-di(hydroxymethyl)propan-1-oic acid. It is also possible to employ polyalkylene imine or polyamido amine based dendrimers.

If those dendrimers according to the invention are used in which branching generations can be designated, use is preferably made of dendrimers of the 2nd or 3rd generation. It is also possible to use dendrimers of a higher generation.

In one embodiment the dentritic polymers sold under the trademark of Boltorn can be used. These dendrimers have been developed by Perstorp (SE 468 771; SE 503 342) and are of polyester type consisting of a multi-functional core, from which branches extend to give a highly branched inherent structure with a large number of terminal hydroxyl groups. The core consists of a polyalcohol, such as trimethylolpropane, pentaerythritol or derivatives thereof. The type of polyol core used governs the number of branches that will extend from it. The hyperbranched structure is built from

2,2-Dimethylol propionic acid (Bis-MPA), which has the unique functionality of one COOH-group and two OH-groups. The shell consists of a large number of OH-groups, where the functionality depends on the type of core used and the number of generations.

5 As indicated above, to at least some of the functional groups of the dendrimer a linking group (chain extender) is attached. At the end of the chain extender a pigment affinic group is present, which interacts with the materials to be dispersed, more in particular with the solid pigments. To the remainder of the functional groups a compatibility-enhancing group will preferably be
10 attached.

 The pigment affinic groups or interacting groups generally comprise a polar group, that has been selected from nitrogen containing moieties, carboxyl moieties, phosphoric ester moieties and sulphonic ester moieties.

 It is important to note that the pigment affinic group is different
15 from the functional group, not only in function but also in chemical nature. The functional group acts to provide a coupling between the core and the outer shell of groups (pigment affinic groups) that provide the adherence to the pigment.

 According to a preferred embodiment a nitrogen containing moiety is
20 used as the pigment affinic group, more in particular a heterocyclic nitrogen moiety. This will be at least a basic (alkaline) nitrogen atom, preferably present in a ring structure (aliphatic or aromatic). Suitable structures have been described in the European patent application Nos. 154.678, 438.836 and 520.586, the contents of which is incorporated herein by way of reference or in
25 WO-A 9726984, the contents of which is incorporated herein by way of reference.

 For this preferred pigment affinic group, the starting point is generally the various aromatic, heterocyclic compounds with one or more nitrogen atoms in the ring, at least one of the nitrogen atoms having a proton.
30 Examples thereof are piperazine, imidazoline, benzimidazole, imidazole,

pyrrolidone, pyrazole, 1,2,4-triazole, benzotriazole, indole, indazole, 1-H-tetrazole, as well as substituted derivatives thereof. Most preferred are pyrrolidone, 1,2,4-triazole, pyrazole, imidazole and derivatives thereof.

Other preferred embodiments include those that are based on acidic
5 moieties like carboxyl moieties, phosphoric ester moieties and sulphonic ester moieties. These embodiments are preferred in case of the use of inorganic pigments and fillers and can be obtained through reaction with cyclic anhydrides, (poly)phosphoric acids, P_2O_5 , SO_2 , and the like.

In addition to the pigment affinic groups, compatibility enhancing
10 groups are preferably present. These groups are attached to the functional groups of the dendrimer, and function to improve the compatibility of the dispersant with the surrounding medium and/or adsorption on solid surfaces. The compatibility enhancing groups can also have a function to influence the solubility of the dispersant in the surrounding medium, i.e. to provide water
15 solubility, water dispersability or solvent solubility.

These compatibility enhancing groups can be selected from fatty materials and derivatives thereof, aromatic materials, optionally substituted alkyl moieties, ester group containing moieties, amide group containing
20 moieties, and ether group containing moieties. Specific examples are polyethers (EO, PO and/or butylenes oxide based), polyesters (polycaprolacton), fatty acids (stearic acid, 12-hydroxy-stearic acid, ricinoic acid), aliphatic chains and aromatic terminated chains. More in particular it is possible to provide aromatic groups on the dendrimer by reacting the functional group thereof with aromatic acids, aromatic alcohols or aromatic
25 amines such as benzoic acid and phthalic acids, naphthol, phenol, aniline, and the like.

In addition to the compatibility enhancing function of these groups they may also have a function to extend the spherical structure of the dispersant.

In a more general formulation, the invention relates to the use of the above-mentioned reaction product as a dispersing agent in liquid formulations such as paints (especially for the automotive industry). Suitable liquid formulations are urethane lacquers, two-component paints, alkyd systems, epoxy coatings, stoving enamels, nitro cellulose paints, acrylics, unsaturated polyester systems, coil coatings, and the like, having dispersed therein solid substances (pigments, fillers).

It is possible to combine the dispersant of the present invention with other dispersing agents and other suitable additives for these formulations.

Through the functional groups, the addition compounds are often capable of forming salts. According to the invention, they can also be used as dispersant in the form of such salts.

These salts are obtained from the dispersant through neutralization with organic or inorganic acids, or bases, or through quaternization. Salts with organic monocarboxylic acids and sulfonic acids are preferred.

The invention will now be explained in and by an example, but is not limited thereto.

Example

A dispersing agent was prepared using the 3-imidazol-1-yl-propionic acid-2-hydroxyethylester described in WO-A-9726984 as the pigment affinic group.

In order to prepare the said ester, at room temperature 40 g of 5-isocyanate-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane (IPDI) and 25.3 g of methoxypropylacetate was weighed into a 500 ml flask.

Next, 44.19 g of 3-imidazol-1-yl-propionic acid-2-hydroxyethylester was added to the flask in 2 hours, under continuous stirring in a nitrogen environment. The exothermic reaction did not exceed the temperature of 60 °C.

After 1 hour the solid content of 70% was measured at 150 °C, using a Mettler HR 73 Halogen Moisture Analyzer.

The final product (B) was a colourless and viscous fluid.

- 5 At room temperature 26.1 g of caprolacton was weighed into a 500 ml flask. The reaction was performed in a nitrogen environment and with continuous stirring. The temperature was raised to 120 °C and at this temperature 25.0 g of Boltorn H20 dentrimer (Perstorp) was carefully added so that the dentrimer dissolved almost immediately.
- 10 Then the temperature was further raised until 170 °C and at this temperature 100 mg of ditbutyltin dilaurate was added to the flask. After 1 hour, 24.0 g of talloil fatty acid (TOFA) was added. As a consequence of this reaction 1.55 g of water was released and was captured by using a dean-stark trap.
- The temperature was decreased until 120 °C when the acid number was less than 5 mg KOH/g. Then, 8.48 g of phthalic anhydride was added and after 1
- 15 hour the temperature was decreased until room temperature. The product was very viscous and had a brown colour.

- At room temperature 25.0 g of the product thus obtained, together with
- 20 100 mg of ditbutyltin dilaurate and 27.05 g of methoxypropylacetate was weighed into a 500 ml flask. Under stirring the said product dissolved in the methoxypropylacetate.

- The reaction was performed in a nitrogen environment and with continuous stirring.
- 25 Carefully, 10.13 g of B was added to the flask in 2 hours, the exothermic reaction did not exceed the temperature of 60 °C.
- After 1 hour, 2.00 g of n-butanol was added and the solid content of 50% was measured at 150 °C. The product was a yellowish liquid with amine value 13.7 mg KOH/g.

In the table below the formulation for the application of the thus obtained product of the invention is given.

<i>Ingredients</i>	<i>Amount (g)</i>
Setal 84-xx-70	10.0
Product of the invention	4.0
Solvesso 100	28.0
Pigment Irgazin red BTR	8.0
Pearls	100

Dispersed for 1,5 hour in a scandex to produce a pigment concentrate

Pigment concentrate	2.50
Setal 84-xx-70	3.91
Setamine 132 BB-71	1.67
Solvesso 100	1.89
E-3031	0.03

Mixed for 30 seconds 3000 rpm with a dispermat

- 5 The lacquer obtained in this way was poured over a polyester sheet and dried for half an hour in the oven at 130 °C. The measured gloss was 89 at $\angle 20^\circ$. The viscosity of the pigment concentrate is given in the table below and was measured with a Brookfield DV-I viscosity meter with spindle #4.

Code	Description	Gloss	
		50 rpm	$\angle 20^\circ$
E-4401	<i>Acrylic dispersant</i>	7920	90.7
Invention	<i>Dendritic polymer</i>	3000	89.1

Claims

1. Dispersing agent or salt thereof, comprising at least one dendrimer, said dendrimer comprising functional groups, that have reacted with a functional moiety, said moiety being defined as -R-X, X being a pigment affinic group, and R being a linking moiety chain having at least 2 atoms in the chain, with the proviso that the functional group and the pigment affinic group are different.
2. Dispersing agent according to claim 1, wherein the functional groups of the dendrimer have been selected from the group of hydroxyl, -NCO, carboxyl and amine.
- 10 3. Dispersing agent according to claim 1 or 2, wherein the pigment affinic group X has been selected from nitrogen containing moieties, carboxyl moieties, phosphoric ester moieties and sulphonic ester moieties.
4. Dispersing agent according to claims 1-3, wherein the linking moiety is linked to the dendrimer and the X-groups through ester, ether, amide, urea or urethane groups.
- 15 5. Dispersing agent according to claims 1-4, wherein the number of functional groups that have reacted with a group R-X is between 5 and 75 % of the total number of functional groups, preferably between 25 and 75 % and more preferred between 50 and 75 %.
- 20 6. Dispersing agent according to claims 1-5, wherein part of the functional groups have reacted with compatibility enhancing groups.
7. Dispersing agent according to claim 6, wherein said compatibility enhancing groups have been selected from fatty materials and derivatives thereof, aromatic materials, optionally substituted alkyl moieties, ester group containing moieties, amide group containing moieties, and ether group containing moieties.
- 25

8. Use of the dispersing agent according to claims 1-5, for dispersing solid substances.
9. Powdered or fibrous solid substances, to be included in liquid systems, which are coated with dispersing agents according to claims 1-5.
- 5 10. Liquid formulation containing a solid substance according to claim 9.
11. Paint, comprising suitable binder material and solid substance according to claim 9.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01F17/00 C08L63/00

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 B01F C08G C08L

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ 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
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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