



Graft polymers of ketone-aldehyde condensation and co-condensation products

The present invention concerns graft polymers of ketone-aldehyde condensation products and co-condensation products and/or the monovalent or polyvalent metal compounds thereof, the production thereof and the use thereof.

Ketone-aldehyde condensation and co-condensation products have long been known. Thus, readily water-soluble condensation products of cycloalkanones and formaldehyde, with the use of sodium sulphite as a substance introducing acid groups, are described for example in DE-AS 23 41 923. However, a serious disadvantage of these condensation products is their low thermal stability, with the result that their range of uses is greatly limited.

The condensation products of aldehydes and ketones containing acid groups according to DE-OS 31 44 673 and co-condensation products according to DE-OS 33 15 152 and the metal compounds of these (co-)condensation products according to DE-OS 34 29 068 have a good thermal stability. Although these products can be used as thickeners, retention agents, surfactants, dispersants or deflocculating agents for aqueous systems, the relevant product properties are not optimum in some fields of use.

It was therefore the object of the present invention to modify the ketone-aldehyde condensation and co-condensation products and the metal compounds thereof in

such a way that the performance characteristics of the corresponding derivatives are further improved.

This object was achieved according to the invention by the provision of graft polymers of ketone-aldehyde condensation and co-condensation products and/or the monovalent or polyvalent metal compounds thereof, which are characterized in that the condensation product consists

- a) of symmetrical or asymmetrical ketones with aliphatic, araliphatic, cyclic or aromatic hydrocarbon residues with at least one non-aromatic residue,
- b) an aldehyde of the formula $R-(CHO)_n$, in which $n = 1$ to 2 and R can be hydrogen or an aliphatic, araliphatic, aromatic or heterocyclic residue and
- c) if desired, of acid groups, preferably carboxy, sulphy, sulphyamido, sulphyoxy, sulphyalkylamine or sulphyalkyloxy groups,

on which anionic and/or non-ionic and/or cationic unsaturated monomers have been grafted.

It has in fact surprisingly turned out that the properties can be influenced in a specific manner by grafting the relevant unsaturated monomers onto the (co-)condensation products or the metal compounds thereof.

The parent structures of the graft polymers according to the invention consist of ketone-aldehyde condensation and co-condensation products and/or the monovalent or



polyvalent metal compounds thereof, as described for example in DE-OS 31 44 673, DE-OS 33 15 152 or DE OS 34 29 068. The ketones used here are symmetrical or asymmetrical compounds with aliphatic, araliphatic, cyclic or aromatic hydrocarbon residues with at least one non-aromatic residue, the total number of carbon atoms and heteroatoms in the ketones preferably being 3 to 12. Suitable aliphatic residues are straight-chained or branched, unsaturated and preferably saturated alkyl residues such as for example methyl, ethyl, propyl, isobutyl, etc.. Araliphatic residues are for example benzyl or phenethyl and aromatic residues are for example α - or β -naphthyl and preferably phenyl.

The ketones can also have one or more substituents such as for example amino, hydroxy, alkoxy, acetyl or alkoxy-carbonyl groups. Examples of ketones with saturated aliphatic residues are acetone, methyl ethyl ketone and methyl isobutyl ketone, examples of ketones with substituted aliphatic residues are methoxyacetone, diacetone alcohol and ethyl acetoacetate, examples of ketones with unsaturated aliphatic residues are methyl vinyl ketone, mesityl oxide and phorone, an example of ketones containing araliphatic residues is benzylacetone, examples of ketones with cyclic residues are cyclohexanone and cyclopentanone and examples of ketones with aromatic residues are acetophenone and 4-methoxyacetophenone.

Suitable aldehydes of the formula $R-(CHO)_n$ are those compounds in which n is 1 to 2 and R is hydrogen, an aliphatic, araliphatic, aromatic or heterocyclic residue and the total number of carbon atoms and heteroatoms preferably assuming a value of 1 to 11. Aliphatic residues are in particular alkyl residues, preferably



having 1 to 6 carbon atoms, such as for example methyl, ethyl, propyl, butyl etc.. The aliphatic residues can also be branched or unsaturated (such as for example vinyl). Aromatic residues are for example α - or β -naphthyl or phenyl and heterocyclic residues are for example furfuryl.

The aldehydes can also have one or more substituents such as for example amino, hydroxy, alkoxy or alkoxy carbonyl groups and/or also if desired, the acid groups present in the condensation products. Aldehydes with more than one aldehyde group, namely in particular dialdehydes can also be used. It is also possible to use the lower saturated aldehydes such as formaldehyde or acetaldehyde in their polymeric form (paraformaldehyde or paraldehyde). Examples of aldehydes with saturated aliphatic residues are formaldehyde (or paraformaldehyde), acetaldehyde (or paraldehyde) and butyraldehyde. Examples of aldehydes with substituted saturated aliphatic residues are methoxyacetaldehyde, 3-methoxypropionaldehyde and acetaldol. Examples of aldehydes with unsaturated aliphatic residues are acrolein and crotonaldehyde. Examples of aldehydes with araliphatic residues are phenylacetaldehyde and phenylpropionaldehyde. Examples of aldehydes with aromatic or heterocyclic residues are benzaldehyde, furfural and 4-methoxyfurfural. For example glyoxal or glutardialdehyde can be used as dialdehydes. Formaldehyde is particularly preferably used as the aldehyde.

The relevant ketone-aldehyde condensation and co-condensation products can if desired, also contain acid groups preferably consisting of carboxy, sulphy, sulphyamido, sulphyoxy, sulphyalkylamine or sulphyalkyloxy groups. An alkyl group in these residues preferably has



1 to 5 carbon atoms and is in particular methyl or ethyl. Inorganic acids such as amidosulphonic acid or their salts such as sodium sulphite, sodium bisulphite and sodium pyrosulphite or organic acids, in particular carboxylic acids such as aminoacetic acid are preferably used as compounds introducing acid groups. The relevant condensation or co-condensation products can also contain two or more different acid groups.

The molar ratio of ketones/aldehydes/compounds introducing acid groups can be varied within wide limits and is as a rule 1 : 0.5 to 18 : 0 to 3. The co-condensation products which are described for example in DE-OS 33 15 152 also contain in addition to the ketone, aldehyde and, if desired, the acid group, 2 to 60 % by weight, preferably 10 to 40 % by weight of a further component selected from the group comprising aminoplast formers and/or a lignin and/or lignite derivative. All common nitrogen-containing compounds in particular those which are suitable for condensation with formaldehyde, can be used in this case as aminoplast formers, in particular urea, melamine, dicyandiamide or a guanamine (preferably acetoguanamine or benzoguanamine).

Phenols which are suitable for the formation of phenol resins i.e. in particular phenol, cresols or xylenols can preferably be used as aromatic compounds, but reactive substituted and/or polynuclear aromatics such as for example naphthalene and derivatives thereof may also be used. The aminoplast formers or aromatic compounds can also be used completely or partially in the form of their pre-condensates or condensation products having different degrees of condensation. Aminoplast formers and aromatic compounds which contain acid groups such as for example naphthalenesulphonic



acids can also be used.

The lignite compounds used may be pure lignite, alkali-treated lignite and/or sulphonated or sulphaalkylated lignite. Within the scope of the present invention, lignin compounds are also understood to include black liquors which are formed during the treatment of wood with sodium sulphite (sulphite process) but also lignin sulphonates and the formaldehyde resins thereof. The lignins or lignites can also be used in the form of their metal compounds (in particular iron and chromium).

Instead of the condensation and/or co-condensation products it is also possible to use the monovalent or polyvalent metal compounds thereof as described in DE-OS 34 29 068. Metal compounds containing metals of groups II A to VIII A and/or of groups I B to V B (according to the definition of Kirk-Othmer, Encyclopedia of Chemical Technology, Interscience Publishers, New York-London-Sydney, 2nd edition 1965, vol. 8, pages 94 to 96) are particularly suitable as metal compounds, the monovalent or polyvalent inorganic or organic salts of these metal being used in particular.

Examples of metal compounds are divalent or tetravalent manganese salts, divalent nickel salts, divalent or tetravalent lead salts, trivalent or hexavalent chromium compounds, divalent or trivalent iron compounds, trivalent aluminium compounds, monovalent and divalent copper compounds, divalent magnesium compounds and trivalent bismuth compounds. The amount of metal in these metal compounds is ≤ 70 % by weight, preferably 0.1 to 20 % by weight. The production of these metal



compounds is described in DE-OS 34 29 068.

It is regarded as essential for the invention that anionic and/or non-ionic and/or cationic unsaturated monomers have been grafted onto these relevant ketone-aldehyde condensation or co-condensation products or the metal compounds thereof.

Vinyl compounds with carboxy, sulpho or phosphoric acid groups are preferably used as anionic unsaturated monomers. Examples of such unsaturated compounds with carboxylic acid groups are acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid and the salts thereof. Examples of vinyl compounds with sulphonic acid groups are vinylsulphonic acid, allylsulphonic acid, methallylsulphonic acid, AMPS, styrenesulphonic acid and the salts thereof. Examples of vinyl compounds with phosphoric acid groups are vinylphosphonic acid, 2-acrylamido-2-methylpropanephosphonic acid and methacryloxyethyl phosphate.

The anionic unsaturated monomer compounds can also be replaced by non-ionic monomers, vinyl or acrylic derivatives being regarded as preferred. In particular N-vinylpyrrolidone, acrylamide, methacrylamide, N,N-dimethylacrylamide, acrolein, mesityl oxide, allyl alcohol, acrylonitrile, vinyl acetate and styrene are used in this case. Further examples of such unsaturated compounds are the esters of the above mentioned unsaturated acids.

Finally for the grafting it is also possible to use cationic unsaturated monomers which are preferably quarternary ammonium compounds. Examples of such



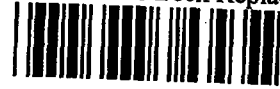


quarternary ammonium compounds are methacroyloxyethyl-trimethylammonium chloride (METAC), (meth)acrylamidopropyltrimethylammonium chloride (MAPTAC), trimethylallyloxyethylammonium chloride (TAAC) and dimethyldiallylammonium chloride (DMDAAC).

The weight ratio of ketone-aldehyde condensation or condensation product to unsaturated monomer can be varied within wide limits, but it has proven to be particularly advantageous to adjust this ratio to 1 : 0.02 to 10. The procedure for the grafting reaction is relatively uncritical and can be carried out by the usual known methods. The grafting reaction is preferably carried out in aqueous solution at a temperature of 0 to 100°C and at a pH of 1 to 13, using conventional free radical initiators based on redox systems such as for example H_2O_2 and iron(II) salts (such as for example iron(II) sulphate heptahydrate), peroxodisulphate/pyrosulphite or sulphite, cerium(IV) salts or thermal initiators such as AIBN or organic or inorganic peroxides.

After the grafting reaction has been carried out which as a rule is complete after a few hours, the reaction solution is preferably rendered neutral with the usual bases or acids. The graft polymer solution formed in this process usually has a solids content of between 5 and 50 % by weight.

Depending on the molecular weight and the type of unsaturated monomer used, the graft polymers according to the invention are suitable as dispersants, retention agents, thickeners and agents for preventing the swelling of clay. Suitable dispersants are usually



short-chained ketone-aldehyde condensation products having a gram-molecular weight of $< 150,000$ and having a high content of acid groups and/or anionic monomers. It is critical in this case that the graft polymer has a negative overall charge. These graft polymers are outstandingly suitable for dispersing inorganic binder suspensions or solutions for example for dispersing Portland Cement, plaster or deep well cement slurries. These products are equally suitable for dispersing clay suspensions and solutions as used for example in drilling fluids in the form of bentonite suspensions.

If the graft polymers according to the invention are used on the basis of long-chained ketone-aldehyde condensation products with a gram-molecular weight of $> 50,000$ and the graft polymers have anionic, non-ionic or cationic charges, these products can be preferably used as retention agents for aqueous systems. These products generally prevent the release of water from water-containing media such as for example concrete, mortar, cement slurries, plaster and anhydrite slurries, clay slurries etc..

The graft polymers according to the invention can also be used as thickeners in particular for aqueous systems, if very long-chained ketone-aldehyde condensation products with a gram-molecular weight of $> 75,000$ are used and the graft polymers have anionic, non-ionic or cationic charges. These products are very suitable for increasing the viscosity of aqueous solutions or suspensions and can be successfully used for example for thickening deep well cement slurries.

Finally the graft polymers according to the invention

can also be used as agents for preventing the swelling of clay in aqueous systems when graft polymers on the basis of short-chained to long-chained ketone-aldehyde condensation products with a gram-molecular weight of 500 to 2,000,000 are used and the graft polymers have cationic or neutral charges. These products prevent for example the swelling of clays such as for example of drilled clay-containing solids in drilling fluids.

By varying the gram-molecular weight and the type of charge it is also possible within the scope of the present invention, to produce products having combined properties.

The following examples are intended to illustrate the invention in more detail. Table 1 gives an overview of the starting materials used in the production examples.

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Table of synthesis examples

Example Ketone	Aldehyde	"Graft basis" Acid group compound	Co- condensation component or metal compound	Graft monomer
A.1 Acetophenone	Paraformaldehyde	Sodium sulphite	-	Acrylic acid
A.2 Diacetone alcohol	Formaldehyde	Sodium sulphite	Urea	Acrylic acid
A.3 Cyclohexanone	Formaldehyde	Sodium sulphite	-	Acrylamide/maleic anhydride
A.4 Acetone	Formaldehyde	Amidosulphonic acid	-	Maleic anhydride
A.5 Acetone	Formaldehyde	Aminoacetic acid	Phenol	Styrenesulphonic acid
A.6 Acetylacetone	Acrolein	Sodium sulphite	-	Methacryloxyethyl phosphate
A.7 Acetophenone	Paraformaldehyde	Sodium sulphite	-	Acrylic acid/vinyl acetate
A.8 Diacetone alcohol	Crotonaldehyde	Sodium pyrosulphite	-	Acrylamidopropionicsulphonic acid
A.9 Acetone	Crotonaldehyde/ Furfural	Sodium sulphite	-	Itaconic acid
A.10 Ethyl methyl ketone	Crotonaldehyde	Aminoacetic acid	-	Acrylamide
A.11 Mesityl oxide	Formaldehyde	Sodium sulphite	-	Acrylamide
A.12 Mesityl oxide	Formaldehyde	Sodium sulphite	-	N,N-Dimethylacrylamide
A.13 Mesityl oxide	Formaldehyde	Sodium sulphite	-	N-Vinylpyrrolidone
A.14 Ethyl methyl ketone	Crotonaldehyde	Aminoacetic acid	-	N-Vinylpyrrolidone
A.15 Acetylacetone	Acrolein	Sodium sulphite	-	Acrolein
A.16 Diacetone alcohol	Formaldehyde	Sodium sulphite	-	Diallyldimethylammonium chloride



Example	"Graft basis"		Co-condensation component or metal compound	Graft monomer
	Ketone	Aldehyde		
A.17	Acetone	Formaldehyde	$\text{Fe}_2(\text{SO}_4)_3$ $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot x\text{H}_2\text{O}$	Acrylic acid
A.18	Mesityl oxide	Formaldehyde	-	N-Vinylpyrrolidone (Starter: AIBN)
A.19	Acetone	Formaldehyde	-	Acrylamidopropionicsulphonic acid (Starter: AIBN)

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A. Synthesis examples

Example A.1

283.0 parts by weight of water,
118.9 parts by weight of sodium sulphite and
84.9 parts by weight of paraformaldehyde
are initially placed in the stated order in a stirred
container with an internal thermometer and reflux
condenser and are heated to 60°C.

113.2 parts by weight of acetophenone are added
dropwise, slowly and uniformly to this initial mixture.
After addition of the ketone, the solution is stirred
for a further 2 hours at 90°C and after cooling to room
temperature, is adjusted to pH 2 with 50 % sulphuric
acid.

The yellow reaction solution is heated to 60°C and air
is displaced from the stirred container by a continuous
stream of nitrogen.

5.8 parts by weight of iron(II) sulphate heptahydrate,
45.0 parts by weight of acrylic acid are added at an
interval of 30 minutes and
2.4 parts by weight of 30 % hydrogen peroxide solution
are added uniformly within 1 minute by means of a
peristaltic pump. Subsequently the reaction solution is
stirred for a further 2 hours at 60°C and, after cooling
to room temperature, is rendered neutral with 35 %
sodium hydroxide solution.

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The brown low-viscosity graft polymer solution has a solids content of 38 % by weight.

Example A.2

119.2 parts by weight of water,
20.0 parts by weight of sodium sulphite,
7.2 parts by weight of urea and
34.6 parts by weight of diacetone alcohol
are placed initially in the stated order in a stirred
container with an internal thermometer and reflux
condenser and are heated to 60°C.

119.1 parts by weight of 30 % formaldehyde are added
dropwise, slowly and uniformly to this initial mixture
so that the temperature increases to 90°C. It is stirred
at 90°C for 1.5 hours and it is diluted with water as
required.

After cooling to room temperature, the viscous solution
is adjusted to pH 2 with 50 % sulphuric acid and heated
to 60°C. Air is displaced from the stirred container by
a continuous stream of nitrogen.

18.5 parts by weight of iron(II) sulphate heptahydrate,
200.0 parts by weight of water, and
14.4 parts by weight of acrylic acid
are added at an interval of 30 minutes and
7.6 parts by weight of 30 % hydrogen peroxide solution
are added uniformly within 1 minute by means of a
peristaltic pump. Subsequently the reaction solution is
stirred for a further 2 hours at 60°C and, after cooling
to room temperature, is rendered neutral with 35 %
sodium hydroxide solution.

The brown highly viscous gel has a solids content of 13 % by weight.

Example A.3

200 parts by weight of water,
84 parts by weight of sodium sulphite and
98 parts by weight of cyclohexanone
are placed successively in the stated order in a stirred container with an internal thermometer and a reflux condenser and are heated to 30°C while stirring vigorously.

A total of 170 parts by weight of formaldehyde solution (30 %) is allowed to flow into this initial mixture from a storage vessel during which the temperature should increase to 90 to 95°C by the end of the formalin addition. After the introduction of the formalin, the solution is kept at 90 to 95°C for a further 2 hours and after cooling to 60°C is adjusted to pH 2 with 50 % sulphuric acid.

The cloudy yellow reaction solution is heated to 60°C and air is displaced from the stirred container by a continuous stream of nitrogen.

33.7 parts by weight of iron(II) sulphate heptahydrate,
15.0 parts by weight of acrylamide and
15.0 parts by weight of maleic anhydride
are added at an interval of 30 minutes and after a further 30 minutes,
13.7 parts by weight of 30 % hydrogen peroxide solution
are added uniformly within 2 minutes by means of a peristaltic pump. Subsequently the reaction solution is



stirred for a further 2 hours at 60°C and, after cooling to room temperature, is adjusted to pH 7 with 35 % sodium hydroxide solution.

The brown low viscosity graft polymer solution has a solids content of 38 % by weight.

Example A.4

246.6 parts by weight of water,
39.9 parts by weight of amidosulphonic acid,
19.3 parts by weight of calcium hydroxide and
47.7 parts by weight of acetone
are placed successively in the stated order in a stirred container with an internal thermometer and reflux condenser and are heated until acetone reflux begins.

A total of 246.6 parts by weight of 30 % formaldehyde solution are allowed to flow into this initial mixture from a storage vessel during which the temperature should increase to 90°C by the end of the introduction of the formalin. After the introduction of the formalin, the solution is kept at 90°C for a further 24 hours and, after cooling to room temperature, is adjusted to pH 2 with 50 % sulphuric acid. The orange coloured solution is heated to 60°C and air is displaced from the stirred container by a continuous stream of nitrogen.

21.3 parts by weight of iron(II) sulphate heptahydrate
and
22.5 parts by weight of maleic anhydride
are added at an interval of 30 minutes and after a further 30 minutes,
8.7 parts by weight of 30 % hydrogen peroxide solution



are added by means of a peristaltic pump within 1 minute.

Subsequently the reaction solution is stirred for a further 2 hours at 60°C and after cooling to room temperature is rendered neutral with 35 % sodium hydroxide solution.

The red-brown low-viscosity graft polymer solution has a solids content of 23 % by weight.

Example A.5

161.3 parts by weight of water,
36.9 parts by weight of solid sodium hydroxide,
34.6 parts by weight of aminoacetic acid,
43.4 parts by weight of phenol and
26.8 parts by weight of acetone
are placed initially in the stated order in a stirred container with an internal thermometer and reflux condenser and are heated until acetone reflux begins.

A total of 138.3 parts by weight of 30 % formaldehyde solution are allowed to flow into this initial mixture from a storage vessel during which the temperature should increase to 95°C by the end of the introduction of the formalin. After the introduction of the formalin, the solution is kept at 95°C for a further 1 hour and, after cooling to room temperature, is adjusted to pH 2 with 50 % sulphuric acid. The orange-red reaction solution is heated to 60°C and air is displaced from the stirred container by a continuous stream of nitrogen.

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26.0 parts by weight of iron(II) sulphate heptahydrate and
60.0 parts by weight of styrenesulphonic acid
are added at an interval of 30 minutes and after a further 30 minutes
11.0 parts by weight of 30 % hydrogen peroxide solution
are added by means of a peristaltic pump within 1 minute.

Subsequently the reaction solution is stirred for a further 2 hours at 60°C and after cooling to room temperature is rendered neutral with 35 % sodium hydroxide solution.

The dark-brown, low-viscosity graft polymer solution has a solids content of 34 % by weight.

Example A.6

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344.3 parts by weight of water,
49.2 parts by weight of acetylacetone and
123.9 parts by weight of sodium sulphite
are placed successively in the stated order in a stirred container with an internal thermometer and reflux condenser and are heated to an internal temperature of 60°C.

A total of 82.6 g of acrolein is added dropwise to this solution. Owing to the highly exothermic reaction, the acrolein is added by a procedure in which the first tenth is added slowly and uniformly and the reaction is then allowed to start which is evident from the onset of yellow colour formation in the initial mixture and increased acetone reflux. The remaining 90 % of the

acrolein is added dropwise while cooling. It is subsequently stirred for 4 hours at 90°C during which the reaction solution becomes deep red.

After the mixture has cooled to room temperature, the pH is adjusted to 2 with 50 % sulphuric acid, the mixture is heated to 60°C and the air is displaced from the reaction container by a continuous stream of nitrogen.

13.2 parts by weight of iron(II) sulphate heptahydrate and

30.0 parts by weight of methacryloxyethyl phosphate are added at an interval of 30 minutes and after a further 30 minutes,

5.4 parts by weight of 30 % hydrogen peroxide solution are added uniformly and continuously within 1 minute by means of a peristaltic pump.

The reaction solution is subsequently stirred for a further 2 hours at 60°C and, after cooling to room temperature, is rendered neutral with 35 % sodium hydroxide solution.

The ochre-coloured graft polymer solution has a solids content of 39 % by weight.

Example A.7

283.0 parts by weight of water,
118.9 parts by weight of sodium sulphite and
84.9 parts by weight of paraformaldehyde
are successively placed in the stated order in a stirred container with an internal thermometer and reflux



condenser and are heated to 60°C.

113.2 parts by weight of acetophenone are added dropwise, slowly and uniformly to this solution so that the internal temperature does not exceed 70°C. After the end of the addition of the ketone stirring is continued for 2 hours at 90°C.

After the mixture has cooled to room temperature the pH is adjusted to 2 with 50 % sulphuric acid, the reaction solution is heated to 60°C and the air is displaced from the reaction container by a continuous stream of nitrogen.

57.4 parts by weight of iron(II) sulphate heptahydrate and
15.0/30.0 parts by weight of vinyl acetate and acrylic acid
are added at an interval of 30 minutes and after a further 30 minutes
22.4 parts by weight of 30 % hydrogen peroxide solution are added uniformly within 1 minute by means of a peristaltic pump.

The reaction solution is then stirred for a further 2 hours at 60°C and, after cooling to room temperature, is rendered neutral with 35 % sodium hydroxide solution.

The brown solution has a solids content of 38 % by weight.

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**Example A.8**

280.0 parts by weight of water,
22.2 parts by weight of sodium pyrosulphite and
27.2 parts by weight of diacetone alcohol
are placed initially in the stated order in a stirred
container with an internal thermometer and reflux
condenser and are heated to 70°C.

12.0 parts by weight of sodium hydroxide and 10.0 parts
by weight of crotonaldehyde are added to the heated
initial mixture. A further 88.0 parts by weight of
crotonaldehyde are added while cooling in such a way
that the internal temperature does not exceed 70°C.
Stirring is continued for 30 minutes at 90°C, the
mixture is cooled to room temperature and the pH is
adjusted to 2 with 50 % sulphuric acid.

The deep red reaction solution is heated to 60°C and air
is displaced from the stirred container by a continuous
stream of nitrogen.

13.6 parts by weight of iron(II) sulphate heptahydrate
and
30.0 parts by weight of acrylamidopropanesulphonic acid
are added at an interval of 30 minutes and
5.6 parts by weight of 30 % hydrogen peroxide solution
are added by means of a peristaltic pump within 1
minute.

The reaction solution is then stirred for a further 2
hours at 60°C and, after cooling to room temperature, is
rendered neutral with 35 % sodium hydroxide solution.



The brown low-viscosity graft polymer solution has a solids content of 34 % by weight.

Example A.9

405.9 parts by weight of water,
42.6 parts by weight of sodium sulphite and
39.2 parts by weight of acetone
are initially placed in the stated order in a stirred container with an internal thermometer and reflux condenser and are heated to 56°C.

A mixture of 64.9 parts by weight of furfural and 47.4 parts by weight of crotonaldehyde is added dropwise to the initial mixture, the internal temperature being kept at 70°C by cooling. After the addition of aldehyde is complete, the mixture is stirred for 4 hours at 90°C, cooled to room temperature and the pH is adjusted to 2 with 50 % sulphuric acid.

The reaction solution is heated to 60°C and air is displaced from the stirred container by a continuous stream of nitrogen.

26.8 parts by weight of iron(II) sulphate heptahydrate,
125.0 parts by weight of water and
37.5 parts by weight of itaconic acid
are added at an interval of 30 minutes and
10.9 parts by weight of 30 % hydrogen peroxide solution
are added uniformly within 1 minute by means of a peristaltic pump.



The reaction solution is then stirred for a further 2 hours at 60°C and, after cooling to room temperature, is rendered neutral with 35 % sodium hydroxide solution.

The brown graft polymer solution has a solids content of 27 % by weight.

Example A.10

346.3 parts by weight of water,
75.7 parts by weight of crotonaldehyde,
38.9 parts by weight of methyl ethyl ketone and
5.4 parts by weight of potassium carbonate
are initially placed in the stated order in a stirred
container with an internal thermometer and reflux
condenser and are stirred for 5 hours at 85°C.

52.5 parts by weight of aminoacetic acid and
43.3 parts by weight of water
are added to the orange solution and
37.9 parts by weight of crotonaldehyde
are added so that the temperature increases to 90°C.
Stirring is continued for 2 hours at 90°C, the mixture
is cooled to 20°C, the pH is adjusted to 2 with 50 %
sulphuric acid and air is displaced from the stirred
container by a continuous stream of nitrogen.

156.4 parts by weight of iron(II) sulphate heptahydrate
and
120.0 parts by weight of acrylamide
are added at an interval of 30 minutes and
64.0 parts by weight of 30 % hydrogen peroxide solution
are added uniformly within 5 minutes by means of a
peristaltic pump.



The reaction solution is stirred for 2 hours at 60°C and after cooling to room temperature, is rendered neutral with 35 % sodium hydroxide solution.

The brown graft polymer solution has a solids content of 31 % by weight.

Example A.11

17.6 parts by weight of water,
43.1 parts by weight of mesityl oxide and
72.1 parts by weight of sodium sulphite
are successively placed in the stated order in a stirred container with an internal thermometer and reflux condenser and are heated to 90°C.

A total of 176.0 parts by weight of 30 % formaldehyde solution are allowed to flow into this initial mixture from a storage vessel, the temperature being kept at between 90 and 95°C by cooling until the end of the introduction of the formalin. After the introduction of the formalin, the solution is kept at 90 to 95°C for a further hour. In order to keep the reaction solution stirrable, it is diluted with water as required.

After cooling to room temperature, the pH is adjusted to 2 with 50 % sulphuric acid. The deep-red reaction solution is heated to 60°C and air is displaced from the stirred container by a continuous stream of nitrogen.

73.0 parts by weight of iron(II) sulphate heptahydrate
and
186.6 parts by weight of acrylamide



are added at an interval of 30 minutes and after a further 30 minutes

29.8 parts by weight of 30 % hydrogen peroxide solution are added while cooling within 10 minutes by means of a peristaltic pump.

The reaction solution is then stirred for a further 2 hours at 60°C and, after cooling to room temperature, is rendered neutral with 35 % sodium hydroxide solution.

The brown graft polymer solution has a solids content of 21 % by weight.

Example A.12

4.6 parts by weight of water,
11.2 parts by weight of mesityl oxide and
18.7 parts by weight of sodium sulphite
are successively placed in the stated order in a stirred container with an internal thermometer and reflux condenser and are heated to 90°C.

A total of 45.7 parts by weight of 30 % formaldehyde solution are allowed to flow into this initial mixture from a storage vessel, the temperature being kept at between 90 and 95°C by cooling until the end of the introduction of the formalin. After the introduction of the formalin, the solution is kept at 90 to 95°C for a further hour. In order to keep the reaction solution stirrable and to dilute the solution to a solids content of about 5 % by weight, 637 parts by weight of water are added successively.

After cooling to room temperature, the pH is adjusted to 2 with 50 % sulphuric acid. The deep-red reaction solution is heated to 60°C and air is displaced from the stirred container by a continuous stream of nitrogen.

0.10 parts by weight of iron(II) sulphate heptahydrate and

36.0 parts by weight of N,N-dimethylacrylamide are added at an interval of 30 minutes and after a further 30 minutes,

4.1 parts by weight of 0.3 % hydrogen peroxide solution are added by means of a peristaltic pump within 1 minute.

The reaction solution is then stirred for a further 2 hours at 60°C and, after cooling to room temperature, is rendered neutral with 35 % sodium hydroxide solution.

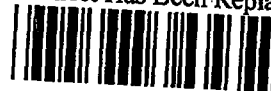
The red graft polymer solution has a solids content of 7 % by weight.

Example A.13

35.2 parts by weight of water,
86.2 parts by weight of mesityl oxide and
144.1 parts by weight of sodium sulphite
are successively placed in the stated order in a stirred container with an internal thermometer and reflux condenser and are heated to 90°C.

A total of 352.0 parts by weight of 30 % formaldehyde solution are allowed to flow into this initial mixture from a storage vessel, the temperature being kept at





between 90 and 95°C by cooling until the end of the introduction of the formalin. After the introduction of the formalin, the solution is kept at 90 to 95°C for a further hour. In order to keep the reaction solution stirrable, it is diluted with water as required.

After the reaction solution has cooled to room temperature, the pH is adjusted to 2 with 50 % sulphuric acid. The deep-red reaction solution is heated to 60°C and air is displaced from the stirred container by a continuous stream of nitrogen.

75.0 parts by weight of iron(II) sulphate heptahydrate and

90.0 parts by weight of N-vinyl-2-pyrrolidone are added at an interval of 30 minutes and after a further 30 minutes

30.6 parts by weight of 30 % hydrogen peroxide solution are added by means of a peristaltic pump within 2 minutes.

The reaction solution is then stirred for a further 2 hours at 60°C and, after cooling to room temperature, is rendered neutral with 35 % sodium hydroxide solution.

The brown graft polymer solution has a solids content of 40 % by weight.

Example A.14

346.3 parts by weight of water,
75.7 parts by weight of crotonaldehyde,
38.9 parts by weight of methyl ethyl ketone and



5.4 parts by weight of potassium carbonate are placed initially in the stated order in a stirred container with an internal thermometer and reflux condenser and are stirred for 5 hours at 80°C.

Subsequently 43.3 parts by weight of water and 52.5 parts by weight of aminoacetic acid are added at 80°C and 37.9 parts by weight of crotonaldehyde are added so that the temperature increases to 90°C.

The reaction solution is stirred for 2 hours at 90°C and, after cooling to room temperature, is adjusted to pH 2 with 50 % sulphuric acid. The reaction solution is heated to 60°C and air is displaced from the stirred container by a continuous stream of nitrogen.

18.1 parts by weight of iron(II) sulphate heptahydrate, 266.7 parts by weight of N-vinylpyrrolidone are added at an interval of 30 minutes and 7.5 parts by weight of 30 % hydrogen peroxide solution are added uniformly within 1 minute by means of a peristaltic pump.

The reaction solution is then stirred for a further 2 hours at 60°C and, after cooling to room temperature, is rendered neutral with 35 % sodium hydroxide solution.

The brown suspension has a solids content of 27 % by weight.



Example A.15

344.3 parts by weight of water,
123.9 parts by weight of sodium sulphite and
49.2 parts by weight of acetylacetone
are initially placed in the stated order in a stirred
container with an internal thermometer and reflux
condenser and are heated to 60°C.

82.6 g of acrolein are added dropwise to this initial
mixture so that the temperature does not exceed 70°C.
After the addition of the aldehyde is complete, the
solution is stirred for a further 4 hours at 90°C and,
after cooling to room temperature, is adjusted to pH 2
with 50 % sulphuric acid.

The deep-red reaction solution is heated to 60°C and air
is displaced from the stirred container by a continuous
stream of nitrogen.

37.7 parts by weight of iron(II) sulphate heptahydrate
and
45.6 parts by weight of acrolein
are added at an interval of 30 minutes and
15.4 parts by weight of 30 % hydrogen peroxide solution
are added uniformly within 1 minute by means of a
peristaltic pump.

The reaction solution is then stirred for a further 2
hours at 60°C and, after cooling to room temperature, is
rendered neutral with 35 % sodium hydroxide solution.



The dark-brown, medium-viscosity graft polymer solution has a solids content of 40 % by weight.

Example A.16

63.3 parts by weight of water,
63.3 parts by weight of 30 % formaldehyde solution,
52.4 parts by weight of diacetone alcohol and
4.5 parts by weight of potassium carbonate
are successively placed according to example 1 in the stirred container and stirred at an internal temperature of 30°C for 8 hours.

28.5 parts by weight of sodium sulphite are added to the yellow solution and heated to 60°C during which the solution becomes red. 72.1 parts by weight of 30 % formaldehyde solution are added dropwise from a storage vessel so that the temperature of the reaction solution increases to 90°C. After the introduction of the formalin, the solution is kept at 90°C for a further hour. In order to keep the solution stirrable, it is diluted with water as required. The viscous solution has a solids content of 14.1 % by weight.

After cooling to room temperature, the pH is adjusted to 2 with 50 % sulphuric acid. The deep-red reaction solution is heated to 60°C and air is displaced from the stirred container by a continuous stream of nitrogen.

0.93 parts by weight of iron(II) sulphate heptahydrate and
90.0 parts by weight of diallyldimethylammonium chloride are added at an interval of 30 minutes and after a further 30 minutes



3.8 parts by weight of 3 % hydrogen peroxide solution are added uniformly within 10 seconds by means of a pipette.

The reaction solution is then stirred for a further 2 hours at 60°C and, after cooling to room temperature, is rendered neutral with 35 % sodium hydroxide solution.

The red, viscous graft polymer solution has a solids content of 18 % by weight.

Example A.17

129.1 parts by weight of water,
54.2 parts by weight of sodium sulphite and
39.9 parts by weight of acetone
are initially placed in the stated order in a stirred container with an internal thermometer and reflux condenser and are heated to 56°C.

As soon as the acetone reflux begins, a total of 258.2 parts by weight of 30 % formaldehyde solution are added dropwise. Owing to the highly exothermic reaction, the first tenth of the formalin solution is added slowly and uniformly. After the reaction has started which is evident from the onset of yellow colour formation in the initial mixture and increased acetone reflux, the remaining formalin is added, the temperature of the mixture being allowed to increase to the boiling point. After the addition of formaldehyde, a 30 minute thermal aftertreatment of the mixture at 95°C is also carried out.

After cooling to room temperature the pH of the solution is adjusted to 4 with acetic acid.

68.6 parts by weight of a 40 % aqueous iron(III) sulphate solution are added to the 29 % resin solution and the mixture is stirred for 2 hours at room temperature during which the pH increases to 8.

For the preparation of the iron-chromium compound, 50.0 parts by weight of a 40 % aqueous solution of sodium dichromate dihydrate are added to the solution of the iron compound and it is stirred again for 2 hours at room temperature. The additions of iron salt and chromium salt correspond to an amount of about 5 % of iron and chromium relative to resin used. The resulting brown solution of the iron-chromium compound has a solids content of 29 %. Its Brookfield viscosity is 17 mPas at room temperature. The pH of the brown resin solution is reduced to 2 with 50 % sulphuric acid. The solution is heated to 60 °C and air is displaced from the stirred container by a continuous stream of nitrogen.

33.7 parts by weight of iron(II) sulphate heptahydrate and
87.3 parts by weight of acrylic acid
are added at an interval of 30 minutes and
13.7 parts by weight of 30 % hydrogen peroxide solution
are added uniformly within 2 minutes by means of a
peristaltic pump. When the hydrogen peroxide is added,
the reaction solution becomes highly viscous.

The reaction solution is stirred for 2 hours at 60°C, diluted with 200 g of water and, after cooling to room temperature, it is neutralized with 35 % sodium



hydroxide solution with the result that the viscosity of the solution again decreases.

The brown graft polymer has a solids content of 30 % by weight.

Example A.18

35.2 parts by weight of water,
86.2 parts by weight of mesityl oxide and
144.2 parts by weight of sodium sulphite
are initially placed in the stated order in a stirred
container with an internal thermometer and reflux
condenser and are heated to 90°C.

352.0 parts by weight of a 30 % formaldehyde solution
are then uniformly added dropwise within 10 minutes
while cooling. After the addition of the formaldehyde,
the solution is stirred for a further hour at 90°C.
After the solution has been adjusted to pH 10 with 50 %
sulphuric acid, it is heated to reflux and air is
displaced from the reaction vessel by passing nitrogen
through the solution for 30 minutes.

A solution of
2.8 parts by weight of 2,2'-azobis-(2-methylpropio-
nitrile) (AIBN) and
180.0 parts by weight of N-vinylpyrrolidone
is added uniformly within 20 minutes to the boiling
initial mixture by means of a peristaltic pump.

The solution is stirred for 3 hours at the boiling point
during which the viscosity increases. After the graft





polymer has cooled to room temperature, it is neutralized to pH 7 with 50 % sulphuric acid.

The red, highly-viscous polymer solution has a solids content of 49 % by weight.

Example A.19

An aldol condensate without an acid group is prepared analogously to the method according to Houben-Weyl, volume 14/II, 1963, page 442, example 3 (a).

696 parts by weight of acetone,
2178 parts by weight of 30 % formaldehyde solution and
20 parts by weight of potassium carbonate dissolved in
35 parts by weight of water
are initially placed in the stated order in a glass beaker.

The clear solution heats up to the boil within 45 minutes. It is allowed to stand for 26 hours and it is then neutralized with concentrated hydrochloric acid. The colourless solution is subsequently evaporated on a rotary evaporator from a solids content of 17 % to about 40 % in order to remove remaining acetone and formaldehyde.

The completely water-soluble resin solution obtained is colourless and has a Brookfield viscosity of 150 mPas and a solids content of 41.4 %.

500 parts by weight of 20 % aldol condensate solution which was prepared by the above method are initially

placed in a stirred container with an internal thermometer and reflux condenser, adjusted to pH 7 with 50 % sulphuric acid and heated to 90°C. Air is displaced from the stirred container by a continuous stream of nitrogen.

A solution of
2.9 parts by weight of 2,2'-azobis-(2-methylpropionitrile) (AIBN) and
100.0 parts by weight of N-vinylpyrrolidone
is added uniformly to the initial mixture within 20 minutes by means of a peristaltic pump.

The solution is stirred for 3 hours at 90°C and diluted with water as required.

The yellow, highly-viscous polymer solution has a solids content of 19 % by weight.

B. Examples of Application

B.1 Dispersing Portland cement

In a dose of 0.5 % by weight relative to the cement content, a graft polymer prepared according to examples A.3 and A.13 increases the degree of spreading of Portland cement of class 35F ($w/c = 0.48$) by 50 % and 40 % respectively at room temperature.

B.2 Dispersing β -hemihydrate plaster

In a dose of 1 % by weight relative to the amount of plaster (302 g of β -hemihydrate plaster, 90 g of water





and 3 g of graft polymer), a graft polymer prepared according to examples A.3 and A.13 increases the degree of spreading by 150 % and 100 % respectively at room temperature. In contrast, the graft basis (cyclohexanone/formaldehyde/sodium sulphite) for example A.3 increases the degree of spreading of the plaster by only 60 %.

B.3 Dispersing deep well cement slurries

The dispersing action of graft polymers according to the invention on deep well cement slurries is shown in Table 2.

The dose of graft polymers is 1.0 % by weight relative to the cement content. The cement slurries consisting of class H cement and water ($w/c = 0.38$) are prepared according to the standard conditions of API RP 10 B and were measured using a Fann 35 SA viscometer at 38°C and four different shear gradients.

Table 2: Decrease in the viscosity by x % at four different shear gradients

Preparation example	Percentage decrease of the Fann viscosity at rpm			
	600	300	200	100
pure cement slurries	0	0	0	0
A.3	-63	-80	-85	-91
A.6	-49	-65	-69	-72
A.13	-69	-83	-88	-93

B.4 Dispersing bentonite suspensions

Bentonite is used as an additive inter alia to improve the removal of drill cuttings in drilling fluids. However, the drilling fluid must remain pumpable in this process i.e. the increase in viscosity due to drilled clays must be controlled from time to time by viscosity-reducing additives. The viscosity-reducing effect of graft polymers according to the invention on an 8 % by weight bentonite suspension is shown in Table 3. The measurement of the rheology was carried out at room temperature using a Fann 35 SA viscometer.

Table 3: Decrease (-) or increase (+) in the viscosity of an 8 % by weight bentonite suspension after the addition of 3 % by weight graft polymer or graft basis

Preparation Examples	Percentage decrease (-) or increase (+) of the Fann viscosity at rpm					
	600	300	200	100	6	3
8 % by weight bentonite suspension	0	0	0	0	0	0
A.1	-54	-78	-82	-85	-90	-90
graft basis A.1	+18	+15	+19	+17	+6	+4
A.5	-47	-67	-69	-75	-83	-83
A.7	-51	-56	-58	-58	-58	-58
graft basis A.7	+18	+15	+19	+17	+6	+4
A.10	-33	-35	-38	-40	-42	-42

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B.5 Thickener for deep well cement slurries

If 1.0 % by weight relative to the cement content, of a graft polymer prepared according to A.4 is added to a class H cement/water slurry ($w/c = 0.38$) which is prepared according to the standard conditions of API SPEC 10, the following viscosity-increasing effect can be measured.

Table 4: Increase in the viscosity by x % at four different shear gradients (38°C)

Preparation example	Percentage increase of the Fann viscosity at rpm			
	600	300	200	100
pure cement slurries	0	0	0	0
A.4	+21	+23	+24	+37
graft basis for A.4	-26	-45	-50	-54

B.6 Thickener for bentonite suspensions

If 3.0 % by weight of graft polymer prepared according to A.13 is added to an 8 % by weight bentonite suspension, the following viscosity-increasing effect can be measured.

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Table 5: Increase in the viscosity by x % of an 8 % by weight bentonite suspension

Preparation Examples	Percentage increase of the Fann viscosity at rpm					
	600	300	200	100	6	3
A.13	+38	+38	+37	+31	24	+24

B.7 Flowing concrete

Graft polymers prepared according to examples A.3, A.6 and A.13 are suitable for the production of flowing concrete according to the "Guidelines for the production and processing of flowing concrete" in the version of May 1974, as cited for example in the Journal "Beton" 24 (1974) on pages 342 to 344.

Table 6: Increase in the degree of concrete spreading in x % at 0.4 % by weight dosage (relative to the cement content)

Example	Percentage increase of the degree of spreading
A.3	35
A.6	31
A.13	33

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B.8 Bonding of gas concrete with mortar or cement paste

Graft polymer prepared according to example A.2 can be used for the preparation of mortar or cement paste with high water retaining capability as, for example for the bonding of gas concrete.

The gas concrete is bonded by the cement paste so firmly that no break occurs in the joint after 24 hours.

B.9 Inhibition of the swelling of clays

Cationic graft polymers according to the invention prevent the swelling of clays. If for example clay-containing drill cuttings from oil wells are introduced into a 2 % by weight aqueous solution of the graft polymer according to example A.16, the pieces of the drill cuttings remain intact. No disintegration or volume increase takes place. In water without the graft polymer according to the invention the particulate drill cuttings undergo swelling. During this the individual particles stick together to form a lump which occupies a multiple of the original inherent volume and finally disintegrates into fine clay particles.

B.10 Retention agent for bentonite suspension

The filtrate water loss of an 8 % by weight bentonite suspension which is determined according to the standard conditions of API 13 B-1 (25°C, 0.7 mPa, 30 minutes) can be reduced by adding 3 % by weight of graft polymer.

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Table 6: Reduction of the API filtrate water loss of an
8 % by weight bentonite suspension

Preparation example	Reduction of the filtrate water loss by %
A.9	-41
A.13	-33

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Claims



1. Graft polymers of ketone-aldehyde condensation and co-condensation products and/or the monovalent or polyvalent metal compounds thereof, characterized in that the condensation product consists
 - a) of symmetrical or asymmetrical ketones with aliphatic, araliphatic, cyclic or aromatic hydrocarbon residues with at least one non-aromatic residue,
 - b) an aldehyde of the formula $R-(CHO)_n$, where $n = 1$ to 2 and R can be hydrogen, an aliphatic, araliphatic, aromatic or heterocyclic residue, and
 - c) if desired, of acid groups, preferably of carboxy, sulpho, sulphamido, sulphony, sulphaalkylamine or sulphaalkyloxy groups, on which anionic and/or non-ionic and/or cationic unsaturated monomers have been grafted.
2. Graft polymers as claimed in claim 1, characterized in that the total number of carbon atoms and heteroatoms in the ketones is 3 to 12.
3. Graft polymers as claimed in claim 1, characterized in that the total number of carbon atoms and heteroatoms in the aldehydes has a value of 1 to 11.
4. Graft polymers as claimed in claims 1 to 3, characterized in that the molar ratio of ketone : aldehyde : acid group is 1 : 0.5 to 18 : 0 to 3.



5. Graft polymers as claimed in claims 1 to 4, characterized in that the co-condensation components for the ketone-aldehyde condensation product are aminoplast formers and/or aromatic compounds or condensation products thereof.
6. Graft polymers as claimed in claim 5, characterized in that the aminoplast former consists of urea, melamine, dicyandiamide or a guanamine.
7. Graft polymers as claimed in claim 5, characterized in that a phenol derivative has been used as the aromatic compound.
8. Graft polymers as claimed in claim 5, characterized in that a naphthalene derivative has been used as the aromatic compound.
9. Graft polymers as claimed in claims 1 to 4, characterized in that the co-condensation component for the ketone-aldehyde condensation product consists of a lignin and/or lignite derivative.
10. Graft polymers as claimed in claims 1 to 9, characterized in that the metal compounds of the condensation and co-condensation products contain metals of group II A to VIII A and/or group I B to V B.
11. Graft polymers as claimed in claims 1 to 10, characterized in that the anionic unsaturated monomers are vinyl compounds with carboxy, sulpho or phosphoric acid groups.





12. Graft polymers as claimed in claims 1 to 10, characterized in that the non-ionic unsaturated monomers are vinyl or acrylic derivatives.
13. Graft polymers as claimed in claims 1 to 10, characterized in that the cationic unsaturated monomers are quaternary ammonium compounds.
14. Graft polymers as claimed in claims 1 to 13, characterized in that the weight ratio of ketone-aldehyde condensation or co-condensation product to unsaturated monomer is 1 : 0.02 to 10.
15. Process for the production of graft polymers as claimed in claims 1 to 14, characterized in that the unsaturated monomers are grafted onto the ketone-aldehyde condensation or co-condensation products in aqueous solution at a temperature of 0 to 100°C.
16. Use of the graft polymers as claimed in claims 1 to 14 as dispersants for inorganic binder suspensions and solutions, for aqueous clay suspensions and solutions or coal/water suspensions, as retention agents, thickeners, in particular for aqueous systems and as agents for preventing the swelling of clay in aqueous systems.
17. Use as claimed in claim 16, characterized in that short-chained ketone-aldehyde condensation products having a gram-molecular weight of < 150,000 and a high content of acid groups and/or anionic monomers are used as dispersants.





18. Use as claimed in claim 16, characterized in that graft polymers on the basis of long-chained ketone-aldehyde condensation products having a gram-molecular weight of $> 50,000$ are used as retention agents and the graft polymers have anionic, non-ionic or cationic charges.
19. Use as claimed in claim 16, characterized in that graft polymers on the basis of very long-chained ketone-aldehyde condensation products having a gram-molecular weight of $> 75,000$ are used as thickeners and the graft polymers have anionic, non-ionic or cationic charges.
20. Use as claimed in claim 16, characterized in that graft polymers on the basis of short-chained to long-chained ketone-aldehyde condensation products with a gram-molecular weight of 500 to 2,000,000 are used as agents for preventing the swelling of clay in aqueous systems and the graft polymers have cationic or neutral charges.

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