

**Sulfinic acid derivatives and their
preparation and use**

The invention relates to sulfinic acid derivatives and
5 their preparation and use in various application areas.

As is known, sulfinic acid, H_2SO_2 , is one of the
strongest known reducing agents. The free sulfinic acid
is unstable. Accordingly, it is only available commer-
10 cially in the form of its stable and correspondingly
manageable derivatives.

The following sulfinic acid derivatives have to date
achieved economic importance:

15

1. Sodium dithionite (fiber bleaching in papermaking,
vat dyeing and textile bleaching, mineral
bleaching, heavy metal reduction in industrial
wastewaters)
- 20 2. Sodium formaldehyde sulfoxylate dihydrate (textile
discharge printing, textile bleaching, redox
cocatalyst in emulsion polymerization, heavy-metal
reduction, pharmaceuticals)
3. Formamidinesulfinic acid (fiber bleaching in
25 papermaking, textile bleaching)
4. Zinc formaldehyde sulfoxylate (textile printing
and textile bleaching)

All of the abovementioned sulfinic acid derivatives are
30 used in the form of aqueous solutions or dispersions.
In aqueous media, sodium dithionite and alkali metal
formamidinesulfinate - the free formamidinesulfinic
acid is virtually insoluble in water and, in its acid
form, has only a very slight reducing action - are only
35 stable for a short time. As a result, even at room
temperature they exhibit an excellent reductive

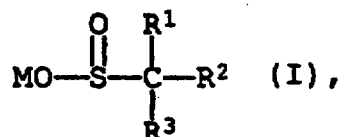
capacity and an excellent bleaching effect on fibers. Aqueous preparations of sodium formaldehyde sulfoxylate and of zinc formaldehyde sulfoxylate are stable at room temperature for months. As a result, both formaldehyde sulfoxylates only exhibit their true reducing action at temperatures above 90° Celsius. In strongly alkaline or acidic media or in the presence of suitably strong oxidizing agents, both formaldehyde sulfoxylates do of course also have a reducing effect at temperatures lower than 90°C. This particular property of the formaldehyde sulfoxylates, namely to exhibit a very uniform and easily controlled reducing effect at temperatures between 5°C and 90°C, is made use of in free-radical-initiated emulsion polymerization. Here, the formaldehyde sulfoxylates are used in various emulsion polymerization systems. In the case of the cold preparation of SBR (styrene butadiene rubber), the polymerization is initiated using organic peroxides. At the low polymerization temperature of about 5°C, the organic peroxides do not, however, decompose into the required free radicals. The peroxide cleavage must be initiated by catalytic amounts of iron(II) salts. The iron in oxidation stage two is converted into oxidation stage three making it no longer suitable for the peroxide cleavage. With the help of the formaldehyde sulfoxylate, the iron(III) ions are again reduced to iron(II) ions - the peroxide cleavage and the free-radical initiation continues. In other emulsion polymerization systems, peroxide compounds, such as hydrogen peroxide or peroxydisulfate, are used as free-radical formers. In order to increase the rate of free-radical formation, reducing agents are again used. Examples which may be mentioned are formaldehyde sulfoxylates, bisulfites, ascorbic acid, isoascorbic acid and sodium erythroate. Formaldehyde sulfoxylates, in particular sodium

formaldehyde sulfoxylate, have proven to be particularly effective and good value reducing agents. During the reduction process, however, the formaldehyde sulfoxylates eliminate formaldehyde. Plastics or
5 polymer dispersions which must not contain formaldehyde are polymerized either using bisulfites, ascorbic acid, isoascorbic acid or sodium erythroate. Since the formaldehyde-free reducing agents are weaker reducing agents, the disadvantage of less complete
10 polymerization compared with formaldehyde sulfoxylates must be accepted. Furthermore, the use of ascorbic acid, isoascorbic acid and of sodium erythroate leads to an undesired yellowing of the polymer.

15 The object of the present invention is to provide novel sulfinic acid derivatives whose chemical properties are as similar as possible to those of formaldehyde sulfoxylate, but which do not eliminate formaldehyde during or after use.

20 Surprisingly, it has now been found that this object is achieved by sulfinic acid derivatives of the type described in more detail below.

25 The present invention thus provides sulfinic acid compounds of the formula (I):



where

30 M is a hydrogen atom, an ammonium ion, a monovalent metal ion or an equivalent of a divalent metal ion of the groups Ia, IIa, IIb, IVa or VIIb of the Periodic Table of the Elements;

R¹ is OH or NR⁴R⁵, where R⁴ and R⁵ independently of one another are H or C₁-C₆-alkyl;

R² is H or an alkyl, alkenyl, cycloalkyl or aryl group, it being possible for these groups to have
5 1, 2 or 3 substituents which are chosen independently of one another from C₁-C₆-alkyl, OH, O-C₁-C₆-alkyl, halogen and CF₃; and

R³ is COOM, SO₃M, COR⁴, CONR⁴R⁵ or COOR⁴, where M, R⁴ and R⁵ are as defined above, or, if R² is aryl,
10 which may be unsubstituted or substituted as defined above, R³ is also H,

and the salts thereof.

15 For the purposes of the present invention, the expressions listed below have the following meanings:

Alkyl represents straight-chain or branched alkyl groups which preferably have 1-6, in particular 1-4,
20 carbon atoms. Examples of alkyl groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-hexyl, etc.

The same applies to the alkyl groups in O-alkyl.

25

Alkenyl represents straight-chain or branched alkenyl groups which preferably have 3-8 carbon atoms, in particular 3-6 carbon atoms. A preferred alkenyl group is the allyl group.

30

Cycloalkyl is, in particular, C₃-C₆-cycloalkyl, cyclopentyl and cyclohexyl being particularly preferred.

35 Aryl (also in aralkyl) is preferably phenyl or naphthyl. If the aryl radical is a phenyl group and is

substituted, it preferably has two substituents. These are, in particular, in the 2- and/or 4-position.

5 Halogen represents F, Cl, Br and I, preferably Cl and Br.

M is preferably an ammonium ion, alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion. Suitable alkali metal ions are, in particular, sodium and potassium ions. Suitable alkaline earth metal ions are in particular magnesium and calcium ions.

R^1 is preferably a hydroxyl or amino group.

15 R^2 is preferably a hydrogen atom or an alkyl or aryl group which may be substituted as above. It preferably has one or two hydroxyl and/or alkoxy substituents.

20 R^3 is preferably either COOM or COOR⁴ (M and R⁴ are as defined above) or, if R^2 is aryl, which may be substituted as stated above, may also be a hydrogen atom.

25 A preferred embodiment covers compounds of the formula (I) in which

M is an alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion;

R^1 is a hydroxyl or amino group; R^2 is H or alkyl; and

30 R^3 is COOM or COOR⁴, where M is H, an alkali metal ion or an equivalent of an alkaline earth metal ion, and R^4 is C₁-C₆-alkyl.

A further preferred embodiment covers compounds of the formula (I), in which

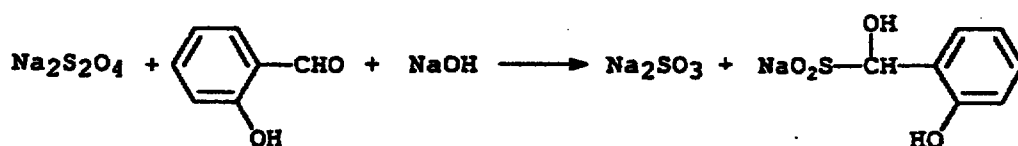
35 M is an alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion;

R¹ is a hydroxyl or amino group;

R² is an unsubstituted aryl or aryl substituted as stated above, in particular hydroxyphenyl or C₁-C₄-alkoxyphenyl; and

5 R₃ is a hydrogen atom.

The novel compounds are prepared from dithionite salts. Advantageously, a salt having a cation which is also desired in the sulfinic acid compounds is used. The
10 dithionite salts are reacted by preparing those compounds in which R² is an unsubstituted or substituted aryl radical and R³ is a hydrogen atom, with the corresponding aromatic aldehyde. This reaction can be illustrated using sodium dithionite and 2-hydroxy-
15 benzaldehyde as an example by the following reaction equation:



All other compounds of the formula M are prepared by reacting the dithionite salts with the corresponding
20 1,2-dicarbonyl compound or a sulfonic acid equivalent thereof. The 1,2-dicarbonyl compound used is, in particular, glyoxylic acid or the corresponding keto compounds and their esters. The reaction can be illustrated using sodium dithionite and glyoxylic acid
25 as an example by the reaction equation below:



The reaction is generally carried out in an aqueous medium in the presence of a base. The aqueous medium may also include water-soluble organic solvents, such
30 as methanol, ethanol, isopropanol, etc. Bases which may be used are, in particular, alkali metal hydroxides and

alkaline earth metal hydroxides. The reaction is generally carried out at ambient temperature; heating of the reaction mixture is generally not required because the reaction is exothermic. The desired product
5 generally precipitates out from the reaction mixture or can be precipitated out by adding polar, water-soluble organic solvents, such as methanol, ethanol, isopropanol, acetone, etc. The resulting product is in the form of the salt which can, if desired, be
10 converted into the free sulfinic acid by acidification or treatment with an acidic ion exchanger.

Furthermore, the product is generally produced in a mixture with the corresponding metal sulfite. In many
15 cases, the mixture also contains the corresponding sulfonic acid and water of crystallization. The novel compounds can be separated off from the accompanying constituents in the usual manner, for example by recrystallization from water or aqueous alcohol.

20 For use in practice, it is not necessary to separate off the accompanying constituents. On the contrary, it has been found that the action of the novel compounds is even increased by these accompanying constituents.
25 The invention thus also provides the corresponding mixtures with the constituents mentioned. For this purpose, the metal sulfite may be present in an amount up to 40% and the sulfonic acid in an amount up to 60%. The water content may be up to 30%.

30 The novel compounds are reducing agents whose reducing action is comparable with that of formaldehyde sulfoxylate. However, they have the advantage of not eliminating formaldehyde before, during and after use.
35 The novel compounds are thus preferentially used in those fields where the evolution of formaldehyde is

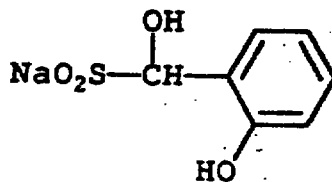
undesired. For example, they can be used as reducing agents in textile printing, in particular in textile discharge printing, in textile bleaching or vat dyeing, or as reducing agents for bleaching minerals, such as kaolin etc., and fibers, for example cellulose fibers. They are preferably used, however, as cocatalyst in emulsion polymerization together with peroxidic initiators in order to allow the polymerization to be carried out at a lower temperature. For this purpose, the sulfinic acids may, if desired, be also used together with oxidizable metal ions, such as Fe^{2+} , Mn^{2+} etc. These metal ions are then advantageously used as counterions to the sulfinic acid compounds, i.e. $\text{M} = \text{Fe}^{2+}$, Mn^{2+} etc.

For use, the novel compounds are generally formulated together with customary additives and auxiliaries. There is no particular limitation in this respect, only that reducing compounds must not be used.

The examples below illustrate the invention without limiting it. The purity figures given in the examples refer to the product which contains water of crystallization which is produced, i.e. the purity is significantly higher when the content of water of crystallization is taken into consideration.

Example 1

2-Hydroxyphenylhydroxymethylsulfinic acid, sodium salt

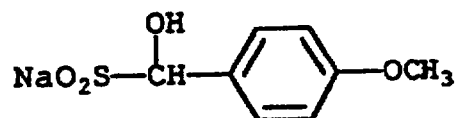


50 ml of 2-hydroxybenzaldehyde and 45 g of 50% strength sodium hydroxide solution were added to an aqueous solution of 90 g of commercially available sodium hydrosulfite (sodium dithionite). After the exothermic reaction had finished, the resulting crude product was separated off using methanol and recrystallized from a methanol/ethanol/water mixture. The 2-hydroxyphenylhydroxymethylsulfonic acid, sodium salt was produced with a purity of 75.8%. The sulfonic acid content was determined using iodometry. The IR spectroscopic data (T = transmission) are as follows:

3551.97 cm^{-1} (28.51 %T); 3175.96 cm^{-1} (19.45 %T); 2915.51 cm^{-1} (29.95 %T); 2747.10 cm^{-1} (34.58 %T); 1899.95 cm^{-1} (61.96 %T); 1682.34 cm^{-1} (44.77 %T); 1641.40 cm^{-1} (38.98 %T); 1594.46 cm^{-1} (32.49 %T); 1505.02 cm^{-1} (42.21 %T); 1455.65 cm^{-1} (17.74 %T); 1387.05 cm^{-1} (27.73 %T); 1330.41 cm^{-1} (40.37 %T); 1280.09 cm^{-1} (30.89 %T); 1244.74 cm^{-1} (23.14 %T); 1200.40 cm^{-1} (31.90 %T); 1155.73 cm^{-1} (30.12 %T); 1111.53 cm^{-1} (29.83 %T); 1098.58 cm^{-1} (32.10 %T); 1072.68 cm^{-1} (28.14 %T); 1030.15 cm^{-1} (16.57 %T); 995.68 cm^{-1} (16.40 %T); 957.46 cm^{-1} (16.83 %T); 872.69 cm^{-1} (43.53 %T); 846.84 cm^{-1} (42.51 %T); 801.62 cm^{-1} (40.51 %T); 762.15 cm^{-1} (28.82 %T); 744.61 cm^{-1} (21.25 %T); 659.92 cm^{-1} (26.13 %T); 629.31 cm^{-1} (30.85 %T); 588.96 cm^{-1} (26.78 %T); 561.45 cm^{-1} (41.13 %T); 496.95 cm^{-1} (30.36 %T).

Example 2

4-Methoxyphenylhydroxymethylsulfonic acid, sodium salt



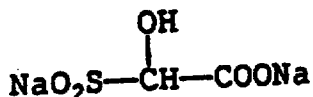
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63 g of 4-methoxybenzaldehyde and 45 g of 50% strength aqueous sodium hydroxide solution were added to 90 g of commercially available sodium hydrosulfite in aqueous solution. Evaporation of the resulting solution precipitated out the crude product. The sodium salt of the sulfonic acid was obtained by crystallization from a methanol/ethanol/water mixture having a purity of 68%. The sodium salt of the corresponding sulfonic acid was present as a secondary constituent.

25

Example 3

2-Hydroxy-2-sulfinatoacetic acid, disodium salt



The reaction of 358 g of commercially available sodium hydrosulfite in 800 ml of water with 268 g of 50% strength glyoxylic acid and 285 g of 50% sodium hydroxide solution gave the 2-hydroxy-2-sulfinatoacetic acid, disodium salt in a yield of 95%. The solid crude product contained 43% of sulfinic acid (without water of hydration). Crystallization from a methanol/ethanol/water mixture gave the hydrate of the sulfinic acid in nice crystals. The sulfur-containing constituents were determined using iodometry. The sulfinic acid shows a reaction with indanthrene paper at about 75°C.

The IR spectrum shows the following peaks:

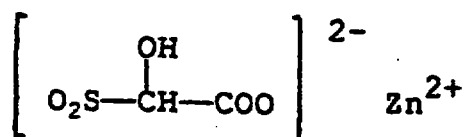
3588.57 cm^{-1} (6.21 μT); 3485.05 cm^{-1} (1.37 μT); 3339.44 cm^{-1} (1.75 μT); 2905.13 cm^{-1} (38.46 μT); 2794.17 cm^{-1} (42.39 μT); 2189.93 cm^{-1} (54.06 μT); 1662.54 cm^{-1} (7.35 μT); 1613.92 cm^{-1} (0.67 μT); 1417.54 cm^{-1} (7.34 μT); 1388.03 cm^{-1} (8.65 μT); 1248.31 cm^{-1} (3.95 μT); 1185.34 cm^{-1} (30.75 μT); 1153.96 cm^{-1} (20.95 μT); 1103.16 cm^{-1} (5.58 μT); 1027.04 cm^{-1} (2.61 μT); 968.33 cm^{-1} (1.77 μT); 938.07 cm^{-1} (26.60 μT); 847.72 cm^{-1} (23.10 μT); 717.14 cm^{-1} (10.46 μT); 645.46 cm^{-1} (14.88 μT); 541.36 cm^{-1} (9.25 μT); 491.77 cm^{-1} (11.95 μT); 445.88 cm^{-1} (19.72 μT).

^{13}C nuclear magnetic resonance spectrum (63 MHz):

δ (ppm): 93.8 (s) ; 177.7 (s)

Example 4

2-Hydroxy-2-sulfinatoacetic acid, zinc salt

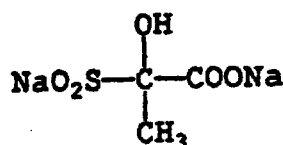


The reaction of 33 g of Zn dust in aqueous medium with sulfur dioxide gave zinc dithionite. This was reacted in situ with 136 g of 50% strength glyoxylic acid.

After the exothermic reaction had finished, 75 g of ZnO were added. The crude product present in the filtrate was precipitated out using methanol and comprised 20% of sulfinic acid and 48% of sulfonic acid (iodometric determination).

Example 5

2-Hydroxy-2-sulfinatopropionic acid, disodium salt



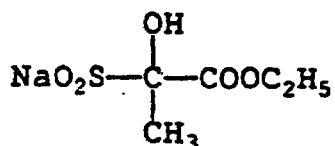
Starting from 89 g of commercially available sodium hydrosulfite in water, the crude product was obtained by reaction with 40 g of pyruvic acid and about 78 g of 50% strength sodium hydroxide solution. The crude product comprised 40% of sulfinic acid and was recrystallized from a methanol/ethanol/water mixture. The content was determined iodometrically. The disodium salt of the corresponding sulfonic acid was present as a secondary constituent.

The IR spectroscopic signals found were as follows:

3484.66 cm^{-1} (6.25 μT); 2995.53 cm^{-1} (26.51 μT); 2758.93 cm^{-1} (32.54 μT); 1592.63 cm^{-1} (0.62 μT); 1456.02 cm^{-1} (16.06 μT); 1436.19 cm^{-1} (17.02 μT); 1397.00 cm^{-1} (4.77 μT); 1367.01 cm^{-1} (7.14 μT); 1190.80 cm^{-1} (2.49 μT); 1038.50 cm^{-1} (0.70 μT); 981.07 cm^{-1} (1.42 μT); 943.83 cm^{-1} (7.90 μT); 857.07 cm^{-1} (20.25 μT); 804.64 cm^{-1} (32.86 μT); 790.68 cm^{-1} (34.62 μT); 710.08 cm^{-1} (30.79 μT); 659.00 cm^{-1} (11.96 μT); 628.53 cm^{-1} (9.93 μT); 558.19 cm^{-1} (26.14 μT); 522.56 cm^{-1} (16.21 μT); 497.03 cm^{-1} (15.70 μT); 431.34 cm^{-1} (28.83 μT).

Example 6

Ethyl 2-hydroxy-2-sulfinatopropionate, sodium salt



After 90 g of commercially available sodium hydrosulfite in aqueous solution had reacted with 60 g of ethyl pyruvate and 39 g of 50% strength sodium hydroxide solution, the ethyl 2-hydroxy-2-sulfinato-propionate, sodium salt precipitated out during the exothermic reaction as the hydrate. The separated off and dried crude product comprises 79% of sulfinic acid (calculated without water of crystallization).

The contents were determined using iodometry. The IR spectroscopic signals can be summarized as follows:

3501.08 cm^{-1} (12.01 %T); 3328.38 cm^{-1} (16.14 %T); 3003.23 cm^{-1} (51.87 %T); 2986.52 cm^{-1} (45.03 %T); 2940.61 cm^{-1} (54.87 %T); 1733.45 cm^{-1} (7.42 %T); 1663.31 cm^{-1} (48.05 %T); 1469.00 cm^{-1} (32.01 %T); 1402.22 cm^{-1} (42.89 %T); 1367.58 cm^{-1} (40.81 %T); 1298.47 cm^{-1} (43.49 %T); 1262.97 cm^{-1} (26.65 %T); 1190.27 cm^{-1} (10.52 %T); 1105.86 cm^{-1} (10.94 %T); 1038.98 cm^{-1} (6.62 %T); 1012.00 cm^{-1} (30.53 %T); 985.42 cm^{-1} (9.37 %T); 948.69 cm^{-1} (28.55 %T); 860.86 cm^{-1} (56.24 %T); 801.55 cm^{-1} (61.53 %T); 685.30 cm^{-1} (51.65 %T); 658.49 cm^{-1} (51.18 %T); 590.17 cm^{-1} (34.18 %T); 523.55 cm^{-1} (34.88 %T); 471.89 cm^{-1} (41.25 %T); 425.61 cm^{-1} (59.75 %T).

Example 7

For the textile discharge printing on a black fabric, a printing paste having the following formulation was chosen.

Base formulation of the printing paste:

434 g of water
100 g of potash
6 g of KL 100 thickener (carboxymethylated starch)
40 g of Lameprint IND8 (guar ether + starch ether)
14 g of glycerol
6 g of Printogen (self-emulsifying mineral oil)

600 g of base formulation

The formaldehyde-free reducing agent corresponding to Example 3 or sodium formaldehyde sulfoxylate for the comparative mixture were then added to this base

formulation.

Mixture 1	Comparative mixture
600 g of base formulation	600 g of base formulation
213 g of 2-hydroxy-2-	107 g of sodium
sulfinatoacetic acid, disodium	formaldehyde sulfoxylate
salt corresponding to Example 3	
(crude product)	

5 The resulting mixtures were then applied to the black fabric next to one another and dried in a drying cabinet. The fabric was then aged at 102°C for 10 minutes, during which time the dye was reduced. The fabric was thoroughly rinsed to remove residues of thickener and other chemicals, and the undyed fabric
10 became apparent at those places where the reducing agent had previously been applied.

15 It is evident that the discharge printing has performed well. The rinsing of the preparations presented no problems of any kind. The disodium salt of 2-hydroxy-2-sulfinatoacetic acid can thus be used in textile discharge printing according to current technology. The results of the discharge printing are summarized in Table 1:

20 Table 1:

Whiteness R457	Mixture 1	Comparative Mixture
1st measurement	69.55	71.40
2nd measurement	70.24	70.73
1st yellowness index	9.83	8.91
2nd yellowness index	9.51	9.05

Example 8

Bleaching of kaolin

The starting concentration of the kaolin was 250 g/l.

The slurry had a pH of 6.5. After the kaolin suspension had been homogenized using a stirrer for 30 minutes, the pH was adjusted to 2.5 using semi-concentrated sulfuric acid.

5

The disodium salt of 2-hydroxy-2-sulfinatoacetic acid corresponding to Example 3 and sodium formaldehyde sulfoxylate were added as 10% strength solutions and were based on the solids content of the kaolin suspension (see Table 2).

10

Reaction conditions:

Temperature: Room temperature

pH: 2.5

15 Reaction time: 2 hours

Table 2:

Kaolin type	Feed amount	Initial whiteness [%]	Final whiteness [%]	Shade R 457	Saturation R 457
	[% , absolutely dry]	R 457	R 457	R 457	R 457
A	0.45 of the disodium salt of 2-hydroxy-2-sulfinatoacetic acid corresponding to Example 3	73.4	76.8	1.51	0.46
A	0.3 of sodium formaldehyde sulfoxylate	73.4	74.5	1.59	0.61
B*	0.3 of the disodium salt of 2-hydroxy-2-sulfinatoacetic acid corresponding to Example 3	79.5	82.5	1.02	0.34
B	0.3 of sodium formaldehyde sulfoxylate	79.5	79.7	1.34	0.46

* Sodium pyrophosphate was added as complexing agent.

5 The preparation containing the disodium salt of 2-hydroxy-2-sulfinatoacetic acid produces good results in the bleaching of kaolin. The preparation containing the disodium salt of hydroxyacetylsulfinic acid reacted 3-4 times more quickly than the sodium formaldehyde sulfoxylate. The use in the bleaching of minerals, in particular for kaolin, is possible according to current technology.

Example 9 (Comparative example)

15 400 g of water, 286 g of a 10% strength aqueous solution of Airvol 205 (polyvinyl alcohol, 88% hydrolysed; DP = 500; manufactured by Air Products and Chemicals, Inc.), 286 g of a 10% strength aqueous solution of Airvol 107 (polyvinyl alcohol, 98% hydrolysed; DP = 500; manufactured by Air Products and Chemicals, Inc.) and 47 g of Igepal CO-887 (nonionic surfactant, manufactured by Rhone-Poulenc, Inc.; 70% strength aqueous solution of Igepal CO-880 comprises approximately 30 mol of ethylene oxide) were charged to a 3.8 liter pressurized reactor and mixed with 4.8 g of a 1% strength aqueous iron(II) sulfate solution. The reaction mixture was adjusted to a pH of 3.3 using 1.75 g of a 50% strength phosphoric acid solution. 1710 g of vinyl acetate monomer were then metered in.

20 The reaction mixture was stirred at 900 rpm and heated to 35°C. 200 g of gaseous ethylene were then introduced at a pressure up to 20.4 atm. 5.7 g of a 10% strength aqueous solution of isoascorbic acid (pH = 4) having the following composition:

35 270 g of water

30 g of isoascorbic acid

0.8 g of 29% strength ammonium hydroxide solution, were then added. The polymerization was initiated using a total of 10 g of 0.65% strength aqueous hydrogen peroxide solution having the following composition:

589 g of deionized water

11.1 g of 35% strength hydrogen peroxide.

After the polymerization had been initiated, the remaining 295.1 g of the ammonium isoascorbate/isoascorbic acid solution were metered in over the course of 4 hours. The remaining 590.1 g of 0.65% strength hydrogen peroxide solution were added to control the polymerization such that the reaction mixture warmed up from 35°C to 55°C over a period of 1 hour and such that the reaction mixture could then be maintained at 55°C for 3 hours. After a total polymerization time of 4 hours, the content of free vinyl acetate monomer was still 1.5%.

The reaction mixture was cooled to 35°C and transferred to a pressureless reactor in order to degas excess ethylene. The free vinyl acetate monomer remaining in the emulsion was subsequently polymerized by the addition of 20 g of a 10% strength aqueous isoascorbic acid solution and a 3.5% strength hydrogen peroxide solution and as a result forced down to a final content below 0.5% of free vinyl acetate monomer. The pH of the polymer emulsion was adjusted to the desired pH (see Table 3) using a 14% strength aqueous ammonium hydroxide solution. The physical properties of the polymer emulsion (latex) are summarized in Table 3.

Example 10 (Comparative example)

The emulsion polymerization as in Example 9 was repeated, and in place of the ammonium isoascorbate/isoascorbic acid, an aqueous solution

consisting of 270 g of water and 22.1 g of sodium formaldehyde sulfoxylate was used. The results are summarized in Table 3.

- 5 Example 11 (cocatalyst in the emulsion polymerization)
The emulsion polymerization as in Example 9 was repeated, and in place of the ammonium isoascorbate/isoascorbic acid, an aqueous solution consisting of 270 g of water and 33 g of reducing agent according to
10 Example 3 (crude product) was used. The results are summarized in Table 3.

Table 3

Parameter of the resulting latices	Example 9 (Comparison)	Example 10 (Comparison)	Example 11 (Invention)
Appearance	slightly yellowish	milky white	milky white
Solids content [%]	62.1	63.4	63.2
pH	6.5	6.0	6.2
Viscosity [Pa·s] (60 rpm; 25°C)	440	380	560
Tg (polymer) [°C]	+5	+4	+7
free formaldehyde [ppm]	-	130	-

- 15 Example 12
Groundwood bleaching
Conditions for the groundwood bleaching:
Stock consistency: 5.4%
Bleaching temperature: 75°C
20 Bleach addition: 0.2/0.4/0.6/0.8/1.0% of bleach,
absolutely dry (based on dry
weight)

Bleaching time: 30 minutes

For the bleaching, 100 g of groundwood were in each case weighed into polyethylene bags. To add the bleach, aqueous solutions were prepared (1 ml of these solutions comprised 0.2% of each bleach absolutely dry). After the bleach solution had been pipetted in, the bags were immediately tied up, and the contents were thoroughly mixed by kneading the closed bags. The bleaching temperature was regulated using a thermostat (water bath).

After the required bleaching time, the pulp slurry was transferred to measuring flasks and the pH after bleaching was measured. The volume was then made up to 300 ml with tap water and the mixture was homogenized by stirring the pulp slurry. The sheets were formed using a customary suction sheet former using the entire pulp slurry. The resulting sheets were vacuum-dried in the sheet former for 12 minutes.

The whiteness R457 of all of the sheets formed was determined using a whiteness measuring device (Elrepho 2000 from Datacolor). The results are summarized in Table 4.

Table 4

Bleach	Amount of bleach [% , absolute ly dry]	Initial pH	Final pH	Whiteness	Whiteness increase ¹⁾
	0.0	6.4	6.3	65.1	-
Sodium	0.2	6.4	6.2	66.6	1.5
formalde-	0.4	6.4	6.2	66.9	1.8
hyde	0.6	6.4	6.2	67.0	1.9
sulfoxylate	0.8	6.4	6.2	67.3	2.2
	1.0	6.4	6.2	67.7	2.6
Disodium salt	0.0	6.5	6.4	65.7	-
of					
2-hydroxy-2-	0.2	6.5	6.4	66.7	1.0
sulfinato-	0.4	6.5	6.5	67.2	1.5
acetic acid	0.6	6.5	6.6	67.6	1.9
corresponding	0.8	6.5	6.6	68.0	2.3
to Example 3	1.0	6.5	6.7	68.1	2.4

¹⁾ Compared with the untreated groundwood

Example 13

5 Deinked pulp bleaching

Conditions for the deinked pulp bleaching:

Stock consistency: 7.4%

Bleaching temperature: 75°C

10 Bleach addition: 0.2/0.4/0.6/0.8/1.0% of bleach,
absolutely dry

Bleaching time: 60 minutes

For the bleaching, 70 g of deinked pulp were in each case weighed into polyethylene bags. To add the bleach, aqueous solutions were prepared (1 ml of these solutions comprised 0.2% of each bleach absolutely dry). After the bleach solution had been pipetted in, the bags were immediately tied up, and the contents were thoroughly mixed by kneading the closed bags. The
20 bleaching temperature was regulated using a thermostat

(water bath).

After the required bleaching time, the pulp slurry was transferred to measuring flasks and the pH after
5 bleaching was measured. The volume was then made up to 300 ml with tap water and the mixture was homogenized by stirring the pulp slurry. The sheets were formed using a customary suction sheet former using the entire pulp slurry. The resulting sheets were vacuum-dried in
10 the sheet former for 15 minutes.

The whiteness R457 of all of the sheets formed was determined using a whiteness measuring device (Elrepho 2000 from Datacolor). The results are summarized in
15 Table 5.

Table 5

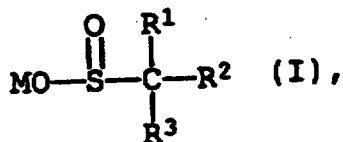
Bleach	Amount of bleach [% absolute ly dry]	Initial pH	Final pH	Whiteness	Whiteness increase ¹⁾
	0.0	7.2	7.2	64.5	-
Sodium	0.2	7.2	7.2	65.9	1.4
formalde-	0.4	7.2	7.3	66.3	1.8
hyde	0.6	7.2	7.3	66.9	2.4
sulfoxylate	0.8	7.2	7.3	66.9	2.4
	1.0	7.2	7.4	67.0	2.5
Disodium salt	0.0	7.2	7.2	64.5	-
of					
2-hydroxy-2-	0.2	7.2	7.4	64.9	0.4
sulfinato-	0.4	7.2	7.4	66.0	1.5
acetic acid	0.6	7.2	7.4	66.2	1.7
corresponding	0.8	7.2	7.5	66.5	2.0
to Example 3	1.0	7.2	7.5	66.3	1.8

¹⁾ Compared with the untreated deinked pulp



We claim:

1. A sulfinic acid compound of the formula (I)



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5 where

- M is a hydrogen atom, an ammonium ion, a monovalent metal ion or an equivalent of a divalent metal ion of the groups Ia, IIa, IIb, IVa or VIIb of the Periodic Table of the Elements;
- 10 R^1 is OH or NR^4R^5 , where R^4 and R^5 independently of one another are H or $\text{C}_1\text{-C}_6\text{-alkyl}$;
- 15 R^2 is H or an alkyl, alkenyl, cycloalkyl or aryl group, it being possible for these groups to have 1, 2 or 3 substituents which are chosen independently of one another from $\text{C}_1\text{-C}_6\text{-alkyl}$, OH, $\text{O-C}_1\text{-C}_6\text{-alkyl}$, halogen and CF_3 ; and
- 20 R^3 is COOM , SO_3M , COR^4 , CONR^4R^5 or COOR^4 , where M, R^4 and R^5 are as defined above, or, if R^2 is aryl, which may be unsubstituted or substituted as defined above, is also H,

and the salt thereof.

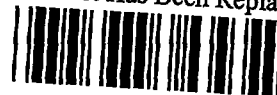
- 25 2. A sulfinic acid compound as claimed in claim 1 of the formula (I),

where

- 30 M is an ammonium or alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion.

3. A sulfinic acid compound as claimed in claim 1 or 2 of the formula (I),

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where

R^1 is OH or NH_2 .

4. A sulfinic acid compound as claimed in claim 1 of
5 the formula (I),

where

R^2 is a hydrogen atom or an alkyl or aryl group
which may have one or two hydroxyl or alkoxy
substituents.

10

5. A sulfinic acid compound as claimed in claim 1 of
the formula (I),

where

R^3 is COOM or COOR⁴, where M and R⁴ are as defined
15 in claim 1.

6. A sulfinic acid compound as claimed in claim 1 of
the formula (I),

where

20 M is an alkali metal ion or an equivalent of an
alkaline earth metal ion or zinc ion;

R^1 is OH or NH_2 ;

R^2 is H or alkyl; and

R^3 is COOM or COOR⁴, M being as defined above and
25 R^4 being H or C₁-C₆-alkyl.

7. A sulfinic acid compound as claimed in claim 4 of
the formula (I),

where

30 R^2 is aryl, which may have one or two hydroxyl
or alkoxy substituents; and

R^3 is H.

8. A sulfinic acid compound as claimed in claim 7 of
35 the formula (I),



where

R^2 is hydroxyphenyl or C_1 - C_4 -alkoxyphenyl.

9. A sulfinic acid compound as claimed in claim 1 of the formula (I),

where

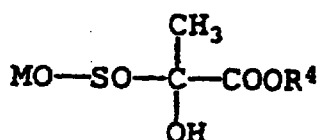
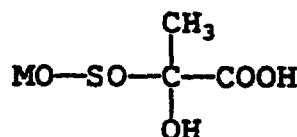
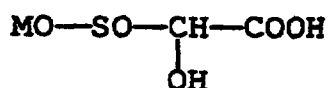
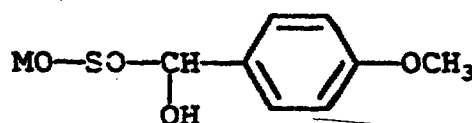
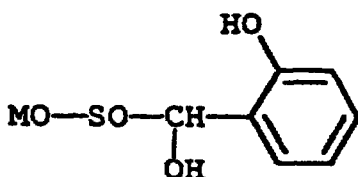
M is an alkali metal ion or an equivalent of an alkaline earth metal ion or zinc ion;

R^1 is OH or NH_2 ;

R^2 is hydroxyphenyl or C_1 - C_4 -alkoxyphenyl; and

R^3 is a hydrogen atom.

10. Compounds of the formulae (M = Na, K, Mg, Ca, Zn):



($R^4 = \text{CH}_3, \text{C}_2\text{H}_5$).

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11. A mixture of a sulfinic acid compound as claimed in one of claims 1 to 10 with the sulfonic acid corresponding to the sulfinic acid compound or the salt thereof and with or without the corresponding sulfite.

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12. A mixture as claimed in claim 11 having the following composition:

5 Compound of the formula (I) 20-99% by weight
Sulfonic acid corresponding to
the compound of formula (I) 0-60% by weight
M₂SO₃ 0-40% by weight

10 13. A mixture as claimed in claim 12 having the following composition:

2-Hydroxyphenylhydroxymethylsulfinic
acid, sodium salt: 61-98% by weight
15 2-Hydroxyphenylhydroxymethylsulfonic
acid, sodium salt: 2-15% by weight
Sodium sulfite: 0-37% by weight

20 14. A mixture as claimed in claim 12 having the following composition:

4-Methoxyphenylhydroxymethylsulfinic
acid, sodium salt: 60-98% by weight
4-Methoxyphenylhydroxymethylsulfonic
25 acid, sodium salt: 2-15% by weight
Sodium sulfite: 0-38% by weight

30 15. A mixture as claimed in claim 12 having the following composition:

2-Hydroxy-2-sulfinatoacetic acid,
disodium salt: 40-73% by weight
2-Hydroxy-2-sulfonatoacetic acid,
disodium salt: 2-7% by weight
35 Sodium sulfite 0-33% by weight

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Water:

5-30% by weight

16. A mixture as claimed in claim 12 having the following composition:

5

2-Hydroxy-2-sulfinatoacetic acid,

zinc salt:

20-70% by weight

2-Hydroxy-2-sulfonatoacetic acid,

zinc salt:

5-60% by weight

10

water:

5-30% by weight

17. A mixture as claimed in claim 12 having the following composition:

15

2-Hydroxy-2-sulfinatopropionic acid,

disodium salt:

38-70% by weight

2-Hydroxy-2-sulfonatopropionic acid,

disodium salt:

5-30% by weight

Sodium sulfite:

0-33% by weight

20

Water:

5-30% by weight

18. A mixture as claimed in claim 12 having the following composition:

25

Ethyl 2-hydroxy-2-sulfinatopropionate,

sodium salt:

60-80% by weight

Ethyl 2-hydroxy-2-sulfonatopropionate,

sodium salt:

0-5% by weight

Sodium sulfite:

0-5% by weight

30

Water:

5-20% by weight.

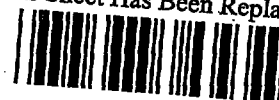
19. A composition comprising at least one sulfinic acid compound as claimed in one of claims 1-10 or at least one mixture as claimed in one of claims 11-18, together with customary additives and auxiliaries.

35



20. The use of the sulfinic acid compound as claimed in one of claims 1-10 as reducing agent.
- 5 21. The use as claimed in claim 20 as cocatalyst in emulsion polymerization or redox catalyst system in plastics production.
- 10 22. The use as claimed in claim 20 as reducing agent component for textile printing, in textile bleaching or vat dyeing or as reducing bleach for mineral refining or fiber finishing.

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