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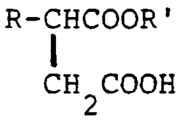
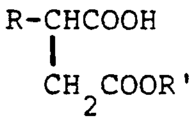
(54) Sizing agent.

(57) A sizing agent for use in paper-making comprises one or more partial esters of alkenylsuccinic acids of the formula (I) and/or (II), namely:-



$$\begin{array}{l}\mathrm{R{-}CHCOOR'}\\ \quad|\\ \quad\mathrm{CH_2COOH}\end{array} \qquad \mathrm{(I)}$$



$$\begin{array}{l}\mathrm{R{-}CHCOOH}\\ \quad|\\ \quad\mathrm{CH_2COOR'}\end{array} \qquad \mathrm{(II)}$$

and/or a salt thereof, in combination with an acid catalyst. Use of such acid catalyst allows lower amounts of sizing agent to be effective.

SIZING AGENT

Background of the Invention

The present invention relates to a sizing agent for use in cellulosic paper-making.

Heretofore a wide variety of sizing agents such as rosin-based, wax-based, alkylketene dimer based, polymer based, alkenylsuccinic anhydride based ones and the like have been proposed for use in paper-making and they all have been actually employed commercially. Since many of these conventional sizing agents are water-insoluble in their nature, it is impossible to use them alone as such so it is usually necessary to disperse and/or emulsify them in water with the aid of an emulsifying agent. However, the emulsifying operation has such drawbacks that it is only achieved with difficulty and that said operation requires additional costs therefor.

For example, Japanese Patent Laid Open No.59-144696(Kawatani) and 59-192798(Satou) describes that a reaction product of maleicanhydride and branched internal olefin having 14-36 carbon atoms were used as a component of a sizing agent.

However the alkenylsuccinic anhydride based sizing agnets in particular undergo hydrolysis with the lapse of time due to their inherent nature if they are kept in contact with water even in short period of time, thereby losing their sizing effect.

Alkenylsuccinic anhydride based sizing agent exerts adequate sizing effect in lower concentrations, thus providing greater economical benefits as compared to that of rosin based, alkenylketene dimer based, wax based sizing agents and the like. However due to the poor stability in water of said alkenylsuccinic anhydrides based sizing agents, they have the serious limitation that the sizing treatment should be finished in a short period of time and this has been the greatest drawback for applying them commercially.

Alkenylsuccinic anhydrides per se are readily absorbed by paper and make the resultant paper water repellant thereby exihibiting a sizing effect. However, once the anhydrides have been hydrolyzed to the corresponding dicarboxylic acids, the resulting dicarboxylic acids are not readily absorbed, thus loosing their sizing effect. In this way,alkenylsuccinic anhydrides have drawbacks in that they drastically change their identity in water the lapse of time, thereby requiring a adequate care.

The inventer has carried out a wide variety of investigations on the sizing effect of alkenylsuccinic acids and their derivatives having various structures, and as a result he has found that unsaturatedhydrocarbyl partial esters of alkenylsuccinic acids and the salts thereof are at least self-emulsifiable with water and provide an excellent sizing effect (Japanese Patent Application No.59-241260).

For example, unsaturated hydrocarbyl diesters of alkenylsuccinic acids not only entail significant difficulties in their synthesis but they also require troublesome procedures for emulsifying similar to conventional sizing agents and further they require additional auxiliaries such as an activator. In addition, they are inferior to unsaturated monohydrocarbyl esters in sizing effect, which makes them useless commercially.

On the other hand, saturated partial(mono)- and di-hydrocarbyl esters of alkenylsuccinic acids have substantially no sizing effect, thus they can not be used as a sizing agent. This is due to the fact that saturated hydrocarbyl mono- and di-esters of alkenylsuccinic acids are not substantially absorbed by paper and also they can only impart poor repellancy to paper.

Therefore, in contrast to saturated esters of alkenylsuccinic acids which are only poorly absobed by paper, thus having no sizing effect, unsaturated hydrocarbyl partial esters of alkenylsuccinic acids have surprisingly been found to be strongly absorbed by paper, making the paper significantly water-repellant, thereby providing an excellent sizing effect along with the advantages that they are not hydrolyzed by water, so that they can maintain their identity as a stable solution or dispersion in water for a long period of time. The unsaturated hydrocarbyl partial esters of alkenylsuccinic acids not only exhibit strong absorbability towards paper, but they alsoshow no discoloring, and indicate a sustained stable sizing effect over a long period of time. Moreover, the unsaturated hydrocarbyl partial esters of the present invention provides consistently stable sized paper sheets.

However even by this sizing agent fairly large amount of the agent is required to achieve a desired sizing effect and cost imposed is not negligible.

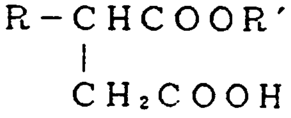
The inventor has carried out a variety of investigation to improve the sizing effect of unsaturated hydrocarbyl partial ester of alkenylsuccinic acid and found that if unsaturated hydrocarbyl partial esters of alkenylsuccinic acids or the water-soluble salt thereof are employed in combination with an acid catalyst, a further improved sizing effect can be obtained. By using the acid catalyst together with the unsaturated partial ester of alkenyl succinic acid as a sizing agent, a quantity of the needed partial ester can be drastically reduced .

The unsaturated hydrocarbyl partial ester of alkenylsuccinic acids of the present invention can be made into a stable emulsified state with cationic starch etc. which have conventionally been used as a spreader. As the alkenyl succinic acid derivatives having various structures, a variety of compounds can be thought of but among them the materials having excellent sizing effect and also superior to conventional sizing agents in handling are the unsaturated hydrocarbyl partial esters.

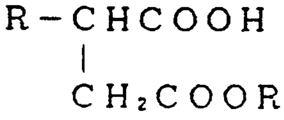
Summary of the Invention

An object of the present invention is to provide a novel sizing agent which consists of unsaturated hydrocarbyl partial ester of alkenylsuccinic anhydride and acid catalist.

More particularly, the present invention relates to a sizing agent for use in paper-making comprising, as an active ingredient, one or more partial esters of alkenylsuccinic acids represented by the following formula (I)and/or (II):



$$\begin{array}{l} R-CHCOOR' \\ \quad | \\ \quad CH_2COOH \end{array} \qquad (I)$$



$$\begin{array}{l} R-CHCOOH \\ \quad | \\ \quad CH_2COOR' \end{array} \qquad (II)$$

and / or one or more salt thereof, wherein R represents an unsaturated hydrocarbyl group having at least 6 carbon atoms and R′ represents an unsaturated hydrocarbyl group having 3 to 18 carbon atoms characterized in that the sizing agent further comprises acid catalyst.

Another object of the present invention is to provide a sizing agent which is at least self-emulsifiable and stable in water for a long period of time and which is effective in lower concentration.

Further object of the present invention is to provide a sizing agent which can be prepared without any difficulties.

Further object of the present invention will become apparent from the descriptions hereinafter referred to.

Detailed Description of the Invention

The most important feature of the present invention is that when sulfonic acids, inorganic acid or Lewis acids are further added into the unsaturated hydrocarbyl partial ester of alkenylsuccinic acid as a catalyst in an amount of 1/100,000-1/10 parts by weight of the ester, the sizing effect can be significantly improved.

Although a reason for this increase in the sizing effect achievable by the use of acid catalyst cannot be fully understood at present, the following assumption may be induced, although this should not be regarded as binding to any particular theory. The acid catalyst such as the sulfonic acid, organic phosphoric acid, inorganic acid or Lewis acid excites the unsaturated linkage in the unsaturated hydrocarbyl partial esters, thereby bringing about a state where the double or triple unsaturated bond can be readily broken, so as to promote the etherification reaction with hydroxyl groups contained in cellulose or the esterification reaction by dehydration and that as a result the fixing of the sizing agent to paper is more fully effected in a short period of time.

The use of the above catalyst can significantly reduce the amount of unsaturated hydrocarbyl partial ester and thus provide great economical adovantages.

The unsaturated hydrocarbyl partial esters of alkenylsuccinic acids can be easily synthesized by a conventional esterification technique. Thus, an alkenylsuccinic anhydride or the corresponding acid and unsaturated alcohol are heated together to cause a reaction between them in the presence or abscence of a catalyst through a ring opening inthe case of anhydride, while in the case of acid through a dehydration to form an unsaturated partial ester. The ratio between the acidic starting material to the unsaturated alcohol is such that the amount of the alcohol is sufficient to esterify only one of the carboxyl groups of the acid.

The alkenylsuccinic anhydride or corresponding acid employed comprises the alkenylsuccinic acid or anhydride in which the alkenyl side chain contains six or more than six carbon atoms and these include, for example, hexenyl-, octenyl-, decenyl-, octadecenyl-, docosenyl-, triacontenyl-, eicosenyl-succinic acid and the like and corresponding anhydrides. As the unsaturated alcohols, there may be mentioned all the unsaturated alcohols having 3 to 18 cabon atoms such as allyl-, propargyl-, butenyl-, butyn-, pentenyl-, hexenyl-, octenyl-, decenyl-, laurenyl-, oleyl-alcohols and the like.

As the acid catalyst, there may be mentioned sulfonic acid, organic phosphoric acid, inorganic acid, such as phosphoric acid, phosphorous acid, hypophosphorous acid, sulfuric acid, nitric acid, hydrochloric acid or the like, a Lewis acid such as boron fluoride, zinc chloride, aluminium chloride, ferric chloride and the like. These acid catalysts can be used alone or two or more in combination.

Among the sulfonic acid catalysts are included benzenesulfonic acid, toluene sulfonic acid, dimethylbenzene sulfonic acid, ethylbenzenesulfonic acid, diethylbenzene sulfonic acid, triethylbenzene sulfonic acid, styrene sulfonic acid, dichlorobenzene sulfonic acid, dichlorotoluene sulfonic acid, aniline sulfonic acid, aminotoluene sulfonic acid, dimethylaniline sulfonic acid, diaminobenzene sulfonic acid, diaminotoluene sulfonic acid, aniline disulfonic acid, aniline-trisulfonic acid, diaminobenzene disulfonic acid, ethyltoluidine sulfonic acid, diethylaniline sulfonic acid, chloroaniline sulfonic acid, aminochlorotoluene sulfonic acid, dichloroaniline sulfonic acid, nitro-benzene sulfonic acid, nitrotoluene sulfonic acid, dinitrobenzene sulfonic acid, dinitrostyrene sulfonic acid, nitrochlorobenzene sulfonic acid, chloronitrotoluene sulfonic acid, dinitrochlorobenzene sulfonic acid, nitroaniline sulfonic acid, phenylhydrazine sulfonic acid, methylphenylhydrazine sulfonic acid, phenol sulfonic acid, cresolsulfonic acid, dihydroxybenzene sulfonic acid, methacryloxybenzenesulfonic acid, aminophenol sulfonic acid, aminomethoxybenzene sulfonic acid, dimethoxyaniline sulfonic acid, chloroaminohydroxybenzene sulfonicacid, nitroaminohydroxybenzene sulfonic acid, butylbenzene sulfonic acid, naphthalene sulfonic acid, naphthalene disulfonic acid, methylnaphthyl sulfonic acid, ethylnaphthyl sulfonic acid, propylnaphthyl sulfonic acid, butylnaphthyl sulfonic acid, lignin sulfonic acid, naphthalene disulfonic acid, naphthalene trisulfonic acid, naphthylamine sulfonic acid, naphthylaminedisulfonic acid, naphthylamine trisulfonic acid, nitronaphthalene sulfonic acid, nitronaphthalene disulfonic acid, nitronaphthalene trisulfonic acid, naphthol sulfonic acid, dihydroxynaphthalene sulfonic acid, naphtholdisulfonic acid, aminonaphtholsulfonic acid, aminonaphtholdisulfonic acid, 1-(4′-amino-2′-chlorobenzoylamino)-8-naphthol-3,6-disulfonic acid, 1-(4′-nitrobenzene)amino-8-naphthol-3,6-disulfonic and nitronaphthol sulfonic acid, anthracene sulfonic acid, anthraquinon sulfonic acid, anthraquinon disulfonic acid, aminoanthraquinon sulfonic acid, diaminoanthraquinon disulfonic acid, nitroanthraquinon sulfonic acid, dihydroanthraquinon sulfonic acid, diaminodioxyanthraquinon sulfonic acid, diaminoanthraquinon disulfonic acid, bromoethane sulfonic acid, 3-fluoromethanesulfonic acid, perchlorooctane sulfonic acid, aminoethanesulfonic acid, hydroxyheptane sulfonic acid, dodecyloxybutane sulfonic acid, propargyloxypropyl sulfonic acid, acetone disulfonic acid, bis[octylsulfonic acid substituted]-sulfonic acid, dihydroxyethane sulfonic acid, mercaptopropane sulfonic acid, methane sulfonic acid, and α-olefine sulfonic acid.

Among the organic phosphoric acid or esters thereof include nitrilotrimethylphosphoric acid, aminodimethyl phosphonomonoethyl-phosphoric acid, ethylene diaminetetramethylphosphoric acid, diethylenetriamine pentamethylphosphoric acid, triethylenetetraminehexamethylphosphoric acid, hydroxyethylidenediphosphoric acid, hydroxypropylidenediphosphoric acid, 1,2,4-tricarboxybutane-2-phosphoric acid, 1,2-dicarboxybutane-2-phosphoric acid, 1,2,4-tricarboxyhexane-1-phosphoric acid, β-chloroethylacidphosphate, bis[(2-hydroxyethyl)methacrylate]acidphosphate, 2-ethylhexyl-acidphosphate, methylacidphosphate, ethylacidphosphate, propylacidphosphate, butylacidphosphate, octylacidphospate, decylacidphosphate, laurylacidphosphate, stearylacidphosphate, dibutylacidphosphate, di(β-chloroethyl)-acidphosphate, di(2-ethylhexyl)acidphosphate, dimethylacidphosphate, diethylacidphosphate, dipropylacidphosphate, dioctylacidphosphate, didecylacidphosphate, dilaurylacidphosphate, distearylacidphosphate, tributylphosphite, tris-(2-ethylhexyl)phosphite, tridecylphosphite, tristearylphosphite, tris(nonylphenyl)-phosphite, trisphenylphosphite, trislauryltrithiophosphite, tris(2,3-dichloropropyl)phosphite, diphenyldecylphosphite, diphenyltridecylphosphite, trimethylphosphite, triethylphosphite, trioctylphosphite, trilaurylphosphite, dilaurylhydrogenphosphite, diphenylhydrogenphosphite, demethylhydrogenphosphite, diethylhydrogenphosphite, depropylhydrogenphosphite, dibutylhydrogenphosphite, dioctylhydrogenphosphite, didecylhydrogenphosphite, distearylhydrogenphosphite. These acid catalysts named are only a part of the present invention and not limited thereto.

The use of the above catalyst can significantly reduce the amount of unsaturated hydrocarbyl partial ester and thus provides great economical advantages.

The amount of acid catalyst to be used in the sizing agent is 0.0001 to 10.0 parts by weight, preferably 0.001 to 1 parts by weight of the acid catalyst per 100 parts by weight of the sizing agent.

The unsaturated partial esters of the present invention can be converted to water-soluble products or at least self-emulsifiable products by converting the remaining free carboxyl group into a salt with alkaline metals or water-soluble amine whereby a stable aqueous solution or dispersion can be obtained by adding it to water. Upon use, it is preferable to use it with a cationic starch, an alkyleneoxide adduct based activator and the like as is conventionally employed in the art to fully assure the benefit of the sizing agent.

The unsaturated hydrocarbyl partial esters of alkenylsuccinic acids of the present invention may be added to paper material in an amount of 0.0001 to 10 parts by weight per 100 parts by weight of paper material (dry base) and preferably 0.01 to 2.0 parts by weight per 100 parts by weight of paper material.

The following Examples will illustrate the present invention, but limited thereto is not the scope of the invention.

Preparation of sizing agent used in examples and comparative examples

(Comparative Example 1 - 15)

In a 4-necked flask 1 mole of dodecenylsuccinic anhydride and 1 mole of allylalcohol were reacted together at 100 ±5 °C for 2 hours to form amonoallyl ester of dodecenylsuccinic acid. The product thus obtained was then converted to its triethanolamine salt which is a viscous yellowish brown liquid having a good self-emulsifiablity in water.

Similarly, monoesters hereinafter described were prepared and these monoesters were subjected to a sizing test in the form of amine salts, sodium salts or potassium salts and like.

(Comparative Examples 16 - 24)

Cationic startch (10 g) was boiled with 90 ml of water at 95-97 °C for 15 minutes to which was added 5 g of the unsaturated monoester of alkenylsuccinic acid set forth in Table 1.

(Comparative Examples 25)

A sizing agent was prepared by modifying the pH of a commercially available rosin based sizing agent to 4.5 with alum.

(Comparative Example 26)

A sizing agent was prepared by adding cationized cellulose to a commercially available alkylketene dimer based sizing agent in an amount of 25 % by weight of the agent.

(Comparative Example 27)

A sizing agent was prepared by mixing 10g of cationic starch with 90ml water, boiling the resulting mixture at 95-97 °C for 15 minutes and then adding 5g of dodecenylsuccinic anhydride thereto.

(Comparative Example 28)

A sizing agent was prepared similar to Comparative Example 1 except that octadecenylsuccinic anhydride acid was used in place of dodecenylsuccinic anhydride.

(Comparative examples 29-30)

Alkenyl succinic anhydrides were mixied with phosphoric acid of the amount shown in the Table .

(Examples 1-70)

A monoallylester of hexenylsuccinic acid was synthesized by reacting in a three-necked flask 1 mole of hexenylsuccinic anhydride and 1 mole of allylalcohol together at 110 ± 5 °C for two hours. To the resultant monoallylester of hexenylsuccinic acid was added 0.1% by weight of benzensulfonic acid on the basis of the weight of the monoallylester. The product thus obtained was modified with cationic starch as to form a homogeneuos slurry.

Similarly additional sizing agents were prepared as set forth in Table 2.

The testing method of sizing degree

The sizing degree of the above mentioned sizing agents was measured under conditions set forth below. Each sizing agent was added to a 0.5% aqueous pulp slurry in an amounts of 0.05, 0.1 and 0.15 % by weight of the sizing agent (solid base) and then mixed together for 15 minutes. The test coditions were as follows:

pulp concentration	0.5%
paper-making procedure	TAPPI STANDARD MACHINE
basis weight	70g/m^2
filler	heavy calcium carbonate
dryng	110 °C for 5 minutes
sizing test	JIS P8122 Stockigt sizing test

The test results thus obtained are reproduced in the following Tables where Table 1 shows the comparative examples and Table 2 shows the examples of the present invention (in each Table succinic acid is abbreviated as s.a.).

Table 1 (Comparative Examples)

Sample		wt. % added		
No.	sizing agent	0.05	0.1	0.2
1	Na salt of monoallylester of hexenyl-s.a.	12	23	30
2	K salt of monopropargyl ester of octenyl-s.a.	11	22	29
3	TEA salt of monooleyl ester of decenyl-s.a.	11	21	29
4	TEA salt of monoallyl ester of dodecenyl-s.a.	12	23	31
5	MEA salt of monobutenyl ester of octadecenyl-s.a.	11	20	29
6	TEtA salt of monohexenyl ester of dodecenyl-s.a.	13	23	30
7	MMtA salt of monolaurenyl ester of octenyl-s.a.	12	22	28
8	TEA salt of monobutinyl ester of octadecenyl-s.a.	11	21	27
9	DEA salt of monopropargyl ester of dodecenyl-s.a.	13	22	29
10	MEA salt of monoallyl ester of octadecenyl-s.a.	13	23	30
11	MEA salt of monoallyl ester of eicosenyl-s.a.	11	20	27
12	DEA salt of monopropargyl ester tetradecenyl-s.a.	11	21	27
13	MEA salt of monobutenylester of triancontenyl-s.a.	12	21	28
14	TEA salt of monopentenyl ester of tetradecenyl-s.a.	12	20	27
15	TEtA salt of monooleyl ester of eicosenyl-s.a.	12	20	28
16	monoallyl ester of dodecenyl-s.a.	12	24	35
17	monopropargyl ester of octadecenyl-s.a.	12	22	32
18	monoallyl ester of eicocenyl-s.a.	12	21	30
19	monolaurenyl ester of octenyl-s.a.	12	23	31
20	monooleyl ester of triancotenyl-s.a.	12	22	30
21	TEA salt of monoallyl ester of dodecenyl-s.a.	13	24	33
22	TEA salt of monopropargyl ester of octenyl-s.a.	13	22	30
23	DEA salt of monopropargyl ester of dodecenyl-s.a.	14	23	32
24	MEA salt of monobutenyl ester of octadecenyl-s.a.	13	22	31
25	rosin based sizing agent	10	14	20
26	alkylketene dimer based siging agent	11	20	27
27	dodecenylsuccinic anhydride	3	9	14

28	octadecenylsuccinic anhydride		4	10	16
29	dodecenylsuccinic anhydride	phosphoric acid 0.1	6	15	21
30	octadecenyl succinic anhydide	phosphoric acid 0.1	7	18	26

Note: TEA: triethanolamine; DEA: diethanolamine; MEA: monoethanolamine
TEtA:triethylamine; MMtA: monomethylamine;

Table 2 (Examples of the present inventtion)

Sample		cat.	Wt.% added		
No.	sizing agent	wt. %	0.05	0.1	0.15
1	monoallylester of hexenyl-s.a.	benzenesulfonic acid 0.1	16	48	59
2	monopropargylester of octenyl-s.a.	naphthylsulfonic acid 0.1	15	42	51
3	monoallyllester of decenyl-s.a.	toluenesulfonic acid 0.2	17	54	63
4	monoallylester of dodecenyl-s.a.	toluenesulfonic acid 0.1	19	61	72
5	monoohexenylester of octadecenyl-s.a.	butylbezenesulfonic acid 0.15	17	58	66
6	monobutenylester of dodecenyl-s.a.	methylnaphthylsulfonic acid 0.1	16	56	65
7	monoallylester of octadecenyl-s.a.	ligninsulfonic acid 0.1	21	66	75
8	monopentenylester of octenyl-s.a.	phosphoric acid 0.1	14	41	50
9	monodecenylester of dodecenyl-s.a.	zinc chloride 0.15	14	42	53
10	monooleylester of docosenyl-s.a.	ferric chloride 0.15	15	46	55

11	monobutenylester of triancotenyl-s.a.	benzenesulfonic acid	0.15	16	51	60
12	monobutynester of eicosenyl-s.a.	diethylbenzenesulfonic acid	0.05	13	39	48
13	monolaurenylester of octadecenyl-s.a.	toluenesulfonic acid	0.2	18	60	71
14	monooctenylester of eicosenyl-s.a.	aluminium chloride	0.3	17	56	63
15	monopropargylester of hexenyl-s.a.	propylnaphthylsulfonic acid	0.05	14	40	50
16	monobutynester of dodecenyl-s.a.	sulfuric acid	0.5	13	36	43
17	monoallylester of octenyl-s.a.	toluenesulfonic acid	0.15	20	63	72
18	monopropargylester of triancotenyl-s.a.	ligninsulfonic acid	0.1	13	40	50
19	monoallylester of octadecenyl-s.a.	phosphoric acid	0.1	16	54	64
20	monopropargylester of hexenyl-s.a.	bromoethanesulfonic acid	0.1	12	32	44
21	monobutenylester of octenyl-s.a.	perchlorooctanesulfonic acid	0.1	12	31	44
22	monoallylester of decenyl-s.a.	aminoethanesulfonic acid	0.15	11	29	40
23	monooleylester of dodecenyl-s.a.	hydroxyheptanesulfonic acid	0.15	11	30	42
24	monopentenylester of octadecenyl-s.a.	dodecyloxypropylsulfonic acid	0.2	12	34	46
25	monoallylester of eicosenyl-s.a.	acetonedisulfonic acid	0.05	11	31	43

26	monohexenylester of triacontenyl-s.a.	dioctylsulfonic acid-substituted-s.a.	0.15	12	33	46
27	monopropargylester of dodecenyl-s.a.	mercaptpropanesulfonic acid	0.2	12	33	45
28	monoallylester of octadecenyl-s.a.	methanesulfonic acid	0.1	11	30	41
29	monoallylester of octenyl-s.a.	dichlorobezenesulfonic acid	0.15	13	36	48
30	monopropargylester of decenyl-s.a.	dichlorotoluenesulfonic acid	0.15	13	35	44
31	monooleylester of hexenyl-s.a	aminotoluenesulfonic acid	0.2	14	40	50
32	monolaurenylester of dodecenyl-s.a.	nitrobezensulfonic acid	0.1	16	43	58
33	monobutenylester of octadecenyl-s.a.	dinitromethylenesulfonic acid	0.1	15	43	57
34	monobutenylester of docosenyl-s.a.	nitrochlorobenzenesulfonic acid	0.15	13	37	45
35	monohexenylester of decenyl-s.a.	dinitrochlorobenzenesulfonic acid	0.15	15	41	51
36	monoallylester of triacontenyl-s.a.	phenolsulfonic acid	0.2	18	55	65
37	monopropargylester of octenyl-s.a.	cresolsulfonic acid	0.2	14	37	50
38	monoallylester of dodecenyl-s.a.	naphthalenedisulfonic acid	0.05	20	60	78
39	monopentenylester of eicosenyl-s.a.	naphthalenetrisulfonic acid	0.05	19	58	77
40	monooleylester of octadecenyl-s.a.	nitronaphthalenedisulfonic acid	0.05	17	56	76

41	monoallylester of octadecenyl-s.a.	naphtolsulfonic acid	0.1	21	61	79
42	monoallylester of dodecenyl-s.a.	aminonaphtholsulfonic acid	0.1	18	59	78
43	monohexenylester of docosenyl-s.a.	anthracenesulfonic acid	0.15	17	55	75
44	monooctenylester of hexenyl-s.a.	anthraquinonesulfonic acid	0.15	17	54	72
45	monooleylester of octenyl-s.a.	anthraquinonedisulfonic acid	0.1	19	59	79
46	monobutenylester of eicosenyl-s.a.	aminoanthraquinonesulfonic acid	0.15	14	38	52
47	monopropargylester of triancontenyl -s.a.	nitroanthraquinonesulfonic acid	0.1	15	39	55
48	monoallylester of dodecenyl-s.a.	hydroxyethilidenediphosphoric acid	0.2	22	65	76
49	monoallylester of octadecenyl -s.a.	1,2,4-tricaboxybutane-2-phosphoric acid	0.1	20	63	75
50	monopropargylester of octenyl-s.a.	1,2—dicarboxybutane-2-phosphoric acid	0.2	19	60	72
51	monooleylester of decenyl-s.a.	nitorilotrimethylphosphoric acid	0.1	16	59	72
52	monobutenylester of hexenyl-s.a.	hydroxypropylidendiphosphoric acid	0.2	21	63	74
53	monoallylester of triancotenyl-s.a.	triethylenetetraminehexamethylphosphoric acid	0.2	17	58	70
54	monopropargylester of octadecenyl-s.a.	phosphorous acid	0.15	12	55	65
55	monopropargylester of dodecenyl-s.a.	hypophosphorous acid	0.15	14	53	64

56	monoallylester of dodecenyl-s.a.	2-ethylhexylacidphosphate	0.1	22	66	77
57	monoallylester of octadecenyl-s.a.	buthylacidphosphate	0.1	23	67	79
58	monopropargylester of decenyl-s.a.	β-chloroethylacidphosphate	0.15	21	64	74
59	monooleylester of hexenyl-s.a.	bis[(2-hydroxyethyl)methacrylate]-acidphosphate	0.15	20	63	72
60	monopropargylester of dodecenyl-s.a.	laurylacidphosphate	0.15	21	65	74
61	monoallylester of octadecenyl-s.a.	dibuthylacidphosphate	0.1	24	65	78
62	monooleylester of hexenyl-s.a.	distearylacidphosphate	0.15	22	64	73
63	monoallylester of dodecenyl-s.a.	di(2-ethylhexyl)acidphosphate	0.15	21	67	78
64	monopropargylester of decenyl-s.a.	di(β-chloroethyl)acidphosphate	0.2	21	65	75
65	monobuthenylester of dodecenyl-s.a.	diocthylacidphosphate	0.1	22	63	74
66	monohexenylester of triancotenyl-s.a.	tributhylphosphite	0.2	17	52	70
67	monopenthenylester of octenyl-s.a.	tristearylphosphite	0.2	15	41	68
68	monooleylester of eicosenyl-s.a.	tris(2,3-dichloropropyl)phosphite	0.15	14	40	66
69	monobuthenylester of octadecenyl-s.a.	diphenyldecylphosphite	0.15	16	51	71
70	monopropargylester of dodecenyl-s.a.	diphenylhydrogenphosphite	0.2	13	39	62

In order to see a change of the sizing degree according to time duration ,sizing tests were carried out. Sizing agents were prepared in the same manner as described above and resultant products were left at room temperature and subjecred to the sizing test being sampled at a constant interval. Testing method are the same as above descrived. The test results are shown in Table 3.

Tabl 3

Sizing Agent	Catalyst	cat.wt %	Stockigt Sizing Degree Hours left			
			0	6	24	48
1. monoallylester of dodecenyl s.a.	2-ethylhexylacidphosphate	0.1	66	63	50	48
2. monoallylester of octadecenyl s.a.	dibutylacidphosphate	0.1	65	63	49	47
3. monopropargylester of decenyl s.a.	beta-chloroacidphosphate	0.15	64	60	48	45
4. monooleylester of hexenyl s.a.	distearylacidphosphate	0.15	64	60	47	44
5. monopentenylester of octenyl s.a.	tristearylphsphite	0.2	41	39	30	29
6. monopropargylester of dedecenyl s.a.	diphenylhydrogenephosphite	0.2	39	36	28	26
7. monobutenylester of octadecenyl s.a.	diphenyldecylphosphite	0.15	51	48	40	38
8. monooleylester of eicosenyl s.a.	tris(2,3-dichloropropyl)phosphite	0.15	40	38	28	26
9. monohexenylester of triacontenyl s.a.	tributylphosphite	0.2	52	47	39	37
(Comparative)						
alkenylsuccinic anhydride						
11. dodecenyl s.a.	--------------------	--	9	1	0	0
12. octadecenyl s.a.	--------------------	--	10	2	0	0

It can be seen from the result of the experiment herein that the product of the present invention is stable and has good resistance to hydrolysis. Indeed, even in an application being left for many hours, the decrease in sizing effect is low due to the good resistance to hydrolysis of the monoester. Many advantages result from this:

a) there is no need to hurry the sizing process after the preparation of the sizing agent;

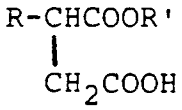
b) the loss of sizing agent is minimized in case of a reopening of an operation after leaving the sizing agent prepared overnight ;

c) longer mixing periods may be utilized which would result in a more homogeneous emulsion of the sizing agent for there is no hydrolysis ;

d) the sizing quality of paper remains stable during many hours continuous sizing operation.

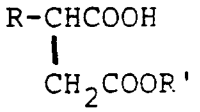
Claims

1. A sizing agent for use in paper-making comprising, as an active ingredient, one or more partial esters of alkenylsuccinic acids represented by the following formula (I) and/or (II):



$$\begin{array}{l} R\text{-}CHCOOR' \\ \;\;| \\ \;\;CH_2COOH \end{array}$$

(I)



$$\begin{array}{l} R\text{-}CHCOOH \\ \;\;| \\ \;\;CH_2COOR' \end{array}$$

(II)

and/or one or more salts thereof, wherein R represents an unsaturated hydrocarbyl group having at least 6 carbon atoms and R′ represents an unsaturated hydrocarbyl group having 3 to 18 carbon atoms characterised in that the sizing agent further comprises an acid catalyst.

2. A sizing agent according to claim 1 wherein said catalyst is selected from a sulfonic acid, an organic phosphoric acid, an inorganic acid, or Lewis acid.

3. A sizing agent according to claim 2 wherein said inorganic acid is selected from phosphoric acid, phosphorous acid, hypophosphorous acid, sulfuric acid, hydrochloric acid, or nitric acid.

4. A sizing agent according to claim 2 wherein said Lewis acid is selected from boron fluoride, zinc chloride, aluminum chloride, or ferric chloride.

5. A sizing agent according to claim 1 wherein said salt is selected from a water soluble amine salt and/or an alkaline metal salt.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 30 4389

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 57, no. 7, January 1987, page 1028, abstract no. 9262, Appleton, WI, US; & JP-A-86 119 798 (CHIYODA CHEMICAL RESEARCH INSTITUTE LTD) 06-06-1986 * Abstract * ---	1,5	D 21 H 3/08
Y	US-A-4 152 312 (G. SACKMANN et al.) * Whole document * ---	1-3,5	
A	US-A-3 655 629 (M. TAKAHARA) * Page 1 * ---	2-5	
A	US-A-2 175 101 (O. ALBRECHT) ---		
A	US-A-3 139 373 (R.W. LIGGETT) ---		
A	EP-A-0 176 479 (CIBA-GEIGY) -----		

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

D 21 H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18-01-1988	NESTBY K.

CATEGORY OF CITED DOCUMENTS

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