(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 116 512**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **84630017.6**

(22) Date of filing: **08.02.84**

(51) Int. Cl.³: **D 21 H 3/02**
D 21 C 9/00, A 61 L 15/00

(30) Priority: **10.02.83 US 465553**

(43) Date of publication of application:
22.08.84 Bulletin 84/34

(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

(71) Applicant: **SHEREX CHEMICAL COMPANY, INC.**
P.O. Box 646 5777 Frantz Road
Dublin, OH 43017(US)

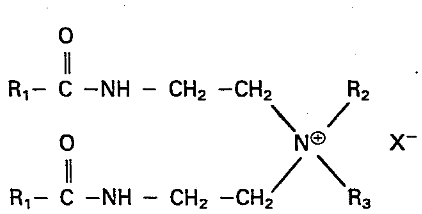
(72) Inventor: **Zeman, William John**
2419 Ruger Avenue
Janesville Wisconsin(US)

(74) Representative: **Schmitz, Jean-Marie et al,**
Office Dennemeyer S.à.r.l. 21-25 Allée Scheffer P.O. Box 41
L-2010 Luxembourg(LU)

(54) Fiber debonder formulation comprising diamido quaternary ammonium compound and alkoxylated fatty acid.

(57) A debonded cellulose fibre pulp web possessing reduced interfibre bonding and reduced mechanical strength is made by blending with an aqueous cellulose pulp slurry, a debonding formulation comprising:

(a) a quaternary ammonium compound having the general formula :



where
R_1 = C_8-C_{30} aliphatic group,
R_2 = (polyoxy alkylene) hydroxyl alkyl group
R_3 = C_1-C_4 alkyl group
X^- = monovalent anion; and
(b) an alkoxylated C_8-C_{30} fatty acid or fatty alcohol.

EP 0 116 512 A1

FIBER DEBONDER FORMULATION COMPRISING DIAMIDO QUATERNARY AMMONIUM COMPOUND AND ALKOXYLATED FATTY ACID

Background of the Invention

The present invention relates to paper debonders and more particularly to a novel paper or fiber debonding formulation.

Due in part to effective advertising, consumers expect soft, fluffy facial tissue and toilet tissue which possesses excellent water absorbency. Additionally, an objective of some major tissue producers is to offer a single-ply bathroom tissue which has the appearance of a standard two-ply tissue in fluffiness, softness, and overall appearance. One method for treating wood pulp to achieve the softness and fluffiness expected by the consumer without losing the ability of the tissue to absorb moisture is to employ a paper debonder during the tissue manufacturing operation. Paper debonders reduce the tensile strength of the tissue by weakening the cellulosic fiber-to-fiber bond. Desirably, the ability of the tissue to absorb moisture is not adversely effected by the paper debonder.

Presently, paper debonders are being employed in two consumer product lines. One line is the disposable tissue (facial and bathroom) product line where debonders are added to the pulp slurry in the wet end of the tissue manufacturing operation. The debonders are expected to provide a finished tissue of improved softness. Disposable diapers are the second consumer product line employing debonders and their use is somewhat different than the use of debonders in disposable tissue production. The paper debonder is added to the pulp slurry at the wet end of the disposable diaper manufacturing operation (ie. at the same manufacturing juncture as in the disposable tissue manufacturing operation), but the debonder functions as a processing aid to assist in the fluffing of the finished paper sheet into the bulky diaper sheeting. The reduced tensile strength of the pulp fibers, thus, aids mechanical pickers in fluffing the dried pulp into a bulky sheeting which is soft yet retains excellent water absorbency.

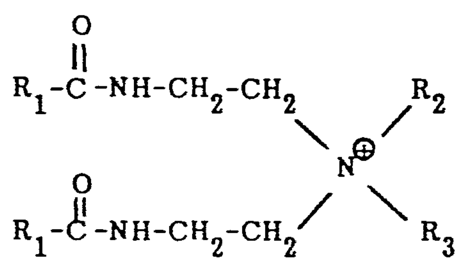
A variety of paper debonders have been employed commercially and proposed in the literature. For example, U.S. Pat. No. 3,554,862 proposes a debonder which is a cationic long-chain fatty alkyl compound having at least 12 carbon atoms in at least one of the alkyl chains while U.S. Pat. No. 3,930,933 employs the same cationic compound in combination with a natural non-drying oil. British Pat. 1,407,134 describes the use of imidazolines as paper debonders. U.S. Pat. No. 4,144,122 proposes the use of bis(alkoxy)-(2-hydroxy propylene) quaternary ammonium compounds which contain both cationic and non-ionic hydrophilic groups as paper debonders. Even though prior paper debonders function effectively in reducing the cellulosic fiber-to-fiber bond, toxicity suspicions concerning them are prevelant.

The present invention is directed to a novel fiber debonding formulation which is not only effective in reducing the cellulosic fiber-to-fiber bond, but also is non-toxic and safe (very low eye and skin irritation).

Broad Statement of the Invention

The present invention is a method for treating cellulosic pulp fibers to reduce interfiber bonding and to reduce the mechanical strength of webs formed therefrom. The method is characterized by blending with an aqueous cellulosic pulp slurry a debonding formulation comprising:

(a)



where $R_1 = C_8$-C_{30} aliphatic group,

R_2 = (polyoxy alkylene) hydroxyl alkyl group

$R_3 = C_1$-C_4 alkyl group

X^- = monovalent anion; and

(b) an alkoxylated C_8-C_{30} fatty acid or fatty alcohol

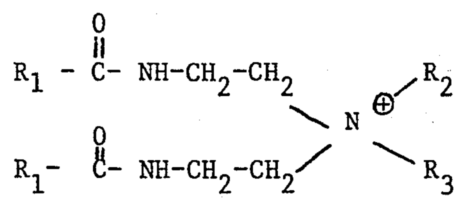
The resulting debonded cellulosic fiber pulp web possessing reduced interfiber bonding and reduced mechanical strength results from the foregoing method and additionally comprises an aspect of the present invention.

Advantages of the present invention include the excellent performance imparted by the paper debonders of the present invention in reducing interfiber bonding and reducing mechanical strength for providing fluffy webs of treated pulp which webs or sheets additionally possess excellent moisture absorbency characteristics. Another advantage is that the ingredients of the debonder formulation are non-toxic and are non-irritants. A further advantage is the debonding formulation is fluid at room temperature and is easily handleable by the fluffed pulp or tissue manufacturer. These and other advantages readily will become apparent to those skilled in the art based upon the disclosure contained herein.

Detailed Description of the Invention

The alkoxylated fatty acids or fatty alcohols employed in the debonding formulation of the present invention traditionally have not been recognized as effective paper debonders themselves. However, in combination, the disclosed quaternary ammonium compounds and alkoxylated fatty acids or fatty alcohols provide a unique (synergistic) fiber debonding formulation which is extremely effective and its effectiveness is quite unexpected based upon the prior art. Thus, it is the unique combination of ingredients comprising the debonding formulation which must be viewed in assessing the present invention rather than the individual ingredients themselves.

Initially, referring to the quaternary ammonium compounds, such quaternary amido ammonium compounds can be represented by the general formula :



In the foregoing general formula, R_1 will comprise a C_8-C_{30} aliphatic group and preferably such groups are hydrocarbyl (fatty) groups. It must be recognized, however, that the occasional presence of oxygen or nitrogen in such substituents may be encountered and their presence is permissible provided that the resulting quaternary ammonium compound in combination with the alkoxylated fatty acid will provide a debonding formulation which possesses the requisite fluidity for use as a paper debonder at commercial scale operations. Thus, preferably R_1 is a C_{12}-C_{18} aliphatic group typically being a fatty group derived from natural and synthetic fatty acids. R_2 comprises a (polyoxy alkylene) hydroxy alkyl group which results from the alkoxylation of the amine nitrogen to which it is attached. Desirably, R_2 will result from the ethoxylation or propoxylation of the amine nitrogen to which it is attached. R_3 preferably is a C_1-C_4 alkyl group and results from the conventional alkylation of a tertiary amine for forming a quaternary ammonium compound. X is a monovalent anion typically encountered in the formation of quaternary ammonium compounds and most often will be halogen, nitrate, acetate, hydroxide, sulfate, or the like though chlorine and sulfate are the most prevelant.

Synthesis of the quaternary ammonium compounds is based upon diethylene triamine (2,2'-diaminodiethylamine). The diethylene triamine molecule is reacted with a C_8-C_{30} carboxylic acid for forming amide groups. Such carboxylic or fatty acids gives rise to the R_1 substituent. The resulting diamidoamine then is alkoxylated in conventional fashion and to such an extent that essentially a 100 percent tertiary amine content results in the reaction mixture. While theoretically only about one mole of alkylene oxide is required for this reaction, generally an excess, eg. up to 50 percent, will be used to ensure the tertiary amine content requirement. As noted above, ethylene oxide and propylene oxide are the reactants of choice and will result in formation of the R_2 substituent. Finally, the diamido tertiary amine molecule is alkylated in conventional fashion to form the resulting quaternary ammonium structure. Alkyl halogens, alkyl nitrates, alkyl sulfates, etc. will be used for this reaction in conventional fashion and will result in the R_3 substituent and the X monovalent anion.The resulting quaternary ammonium compound can be cut in an alcohol, glycol, or similar solvent for increasing its handling characteristics and/or to supply a desired actives concentration of the quaternary ammonium compound for formulating the debonder formulation of the present invention. The proportion of quaternary ammonium compound in the ultimate debonding formulation generally will be from between about 10% or 50% by weight of the debonding formulation.

Referring to the alkoxylated C_8-C_{30} fatty acid or fatty alcohol,the fatty acids or alcohols are conventional in nature broadly ranging from C_8-C_{30} fatty acids or alcohols, advantageously C_{12}-C_{22} and preferably C_{18} fatty acids or alcohols. The fatty acids or alcohols are alkoxylated in conventional fashion, advantageously with ethylene oxide, though propylene oxide, butylene oxide, and other conventional alkylene oxides may be used in this reaction scheme. The proportion of alkoxy groups generally should be from between about 2 and 12 moles of alkoxy group per mole of fatty acid or alcohol and advantageously from between about 4 and 7 moles per mole of fatty acid or alcohol. The proportion of alkoxylated fatty acid or alcohol in the debonding formulation will range from between about 90% to 50% by weight of the debonding formulation.

The debonding formulation optionally may contain minor proportions of solvents for improving the fluidity and handling characteristics of the debonding formulation. For example, propylene glycol or the like may be used in the debonding formulation for improving handling characteristics of the debonding formulation without imparting any adverse effects to the debonded pulp. Additional such fluidity-improving solvents include, for example, alkanols, other alkylene glycols, ethers and the like. When the fluidity-enhancing solvents are used in the formulation, the proportion of alkoxylated fatty acid or alcohol is reduced to accommodate such solvents for providing between about 40 and 60weight percent alkoxylated fatty acid or alcohol and between about 5 and 20 percent fluidity-enhancing solvent.

In practicing the present invention, the debonding formulation is manufactured readily by mechanical blending of the quaternary ammonium compound and alkoxylated fatty acid or fatty alcohol in conventional fashion, optionally also containing a fluidity-enhancing solvent. The debonding formulation is applied to an aqueous pulp slurry in conventional fashion. The type of pulp employed is not a limitation on use of the debonding formulations and can be conventional Kraft pulp or sulfite pulp.The debonding formulation is added to the aqueous slurry in a proportion of between about 0.1 and 2% (by weight of the dry pulp solids),advantageously from between about 0.2 and 1%, and preferably between about 0.2 and 0.4 weight percent. As noted above, the pulp slurry can be intended for tissue production, disposable diaper production, or any other cellulosic fiber product wherein reduced tensile strength is desired. Preferably, the pulp slurry will be fluffed for production of disposable diapers, sanitary absorbents, and the like.

The following examples show how the present invention can be practiced but should not be construed as limiting. In this application, all percentages and proportions are by weight and all units are in the metric system, unless otherwise expressly indicated. Also, all citations are expressly incorporated herein by reference.

<u>IN THE EXAMPLES</u>

50g of wood pulp (Albacel Bleached Kraft or Puget S Bleached

Sulfite) for each debonder evaluated was placed in a TAPPI Standard 300 rpm disintegrator having a 4 L capacity. Approximately 3L of tap water was added and allowed to disperse in the wood pulp for about 5 minutes. The debonder sample then was added at a rate of either 1.5 or 4.0 g/kg of pulp and agitation continued for an additional 2 minutes. The slurry from the disintegrator was diluted with tap water for use in hand sheet production. The hand sheets (nominally at 60 g/m^2) were produced in a TAPPI sheet mold. The sheets were removed from the mold and pressed between dry blotters at a pressure of 3.5 kg/cm^2 (50 psi) for a period of 5 minutes on a first press followed by 2 minutes on a second press. The pressed sheets then were placed in TAPPI drying ring which were housed under standardized conditions of a constant temperature of 21.1^o C (70^{o}F) and 50% relative humidity for drying overnight.

The conditioned hand sheets were tested in accordance with standard test methods set forth below :

(a) Hand sheet formation, TAPPI test method T 205 om-81;

(b) Physical testing of hand sheets, TAPPI test method T 220 os-71;

(c) Z-directional tensile test, TAPPI test method T 506 su-68; and

(d) Absorption of water by lightweight creped paper, Canadian test method CPPA F.7P(PM-74).

EXAMPLE 1

Debonder candidates were formulated as follows:

DEBONDER

Sample No.	wt.-%	Ingredient
Control	—	none
SC61-26	30.0	*Diamido-ethoxylated-methyl ammonium methylsulfate
	70.0	4-mole ethoxylated of oleic acid
SC61-27	30.0	*Diamido-ethoxylated-methyl ammonium methylsulfate
	70.0	7-mole ethoxylated of oleic acid
SC61-28	30.0	**Diamido-propoxylated-methyl ammonium methylsulfate
	70.0	4-mole ethoxylate of oleic acid
SC61-29	30.0	**Diamido-propoxylated-methyl ammonium methylsulfate
	70.0	7-mole ethoxylate of oleic acid

*90% solids in isopropanol of bis(tallowamidoethyl)-(2-hydroxyethyl)-methyl ammonium methylsulfate

**90% solids in isopropanol of bis(tallowamidoethyl)-(2-hydroxy propyl)-methyl ammonium methylsulfate

The debonders were added to the pulp at the rate of 1.5 g per kilogram of pulp. The pulp was softwood Kraft pulp (Albacel) for the first text series and softwood sulfite pulp (Puget S) for the second test series. The following test results were recorded.

TABLE 1

KRAFT PULP

Test	Sample No.				
	Control	SC61-26	SC61-27	SC61-28	SC61-29
TAPPI Handsheet, 2000 cm^2(g)	1.25	1.09	1.11	1.17	1.11
Grammage (g/m^2)	62.5	54.5	55.5	58.5	55.5
Caliper (mm)	0.124	0.111	0.114	0.115	0.110
Apparent Density (g/cc)	0.504	0.491	0.487	0.509	0.505
Bulk (cc/g)	1.98	2.04	2.05	1.96	1.98
Mullen Burst (kPa)	122	28.9	30.3	28.2	22.7
Tear Strength (mN/16 ply)	1300	665	753	703	665
Tensile Strength (kg/m)	201	115.9	113.3	110.7	98.7
Breaking Length (km)	3.220	2.127	2.041	1.892	1.778
Tensile,Z-directional (kPa)	0.322	0.238	0.216	0.215	0.215
Absorbency Time (sec/5 O.D.,g.)	1.90	1.80	1.85	1.75	1.75

TABLE 2

SULFITE PULP

Test	Sample No.				
	Control	SC61-26	SC61-27	SC61-28	SC61-29
TAPPI Handsheet, 2000 cm^2(g)	1.17	1.13	1.04	1.17	1.18
Grammage (g/m^2)	58.6	56.3	52.0	58.3	59.1
Caliper (mm)	0.115	0.120	0.110	0.124	0.124
Apparent Density (g/cc)	0.507	0.471	0.475	0.474	0.476
Bulk (cc/g)	1.97	2.12	2.11	2.11	2.17
Mullen Burst (kPa)	40.4	26.9	16.2	27.8	27.7
Tear Strength (mN/16 ply)	546	418	358	421	471
Tensile Strength (kg/m)	69.1	46.5	42.4	49.7	49.3
Breaking Length (km)	1.179	0.826	0.815	0.853	0.835
Tensile,Z-directional (kPa)	0.197	0.184	0.148	0.176	0.149
Absorbency Time (sec/5 O.D.,g.)	16.75	9.70	7.90	7.95	6.75

The above-tabulated results show the debonding effect achieved by the debonder formulation of the present invention. In order to place this data in an easier to understand form, the percentage loss in strength of the handsheets is given below:

TABLE 3

Test	Sample No. (% loss)			
	SC61-26	SC61-27	SC61-28	SC61-29
Kraft				
Mullen Burst	76.3	75.2	76.9	81.4
Tear Strength	48.8	42.1	45.9	48.8
Tensile Strength	42.3	43.6	44.9	50.9
Z-Tensile	26.1	32.9	33.2	33.2
Sulfite				
Mullen Burst	33.4	59.9	31.2	31.4
Tear Strength	23.4	34.4	22.9	13.7
Tensile Strength	32.7	38.6	28.1	28.7
Z-Tensile	6.6	24.9	10.7	24.4

The above-tabulated results demonstrate the strength decrease imparted by the novel debonder formulation. Even though the overall strength decreased significantly, the water absorbency rate remained substantially constant.

EXAMPLE 2

Next, in order to demonstrate the synergistic effect achieved by combining the diamido-ammonium quaternary debonder with the alkoxylated fatty acid, debonder formulations with and without the alkoxylated fatty acid were evaluated at a dosage of 4g/kg of pulp.

The debonder formulations appear below:

Sample No.	wt.-%	Ingredient
Control	——	None
SC61-53	30.0	bis(cleylamidoethyl)-(2-hydroxyethyl)-methyl ammonium methylsulfate
	70.0	isopropanol
SC50-40F	30.0	bis(oleylamidoethyl)-(2-hydroxyethyl)-methyl ammonium methylsulfate
	70.0	7-mole ethoxylate of oleic acid

TABLE 4

KRAFT PULP

Test	Sample No.		
	Control	SC61-53	SC50-40F
TAPPI Handsheet, 2000 cm^2(g)	1.12	1.24	1.24
Grammage (g/m^2)	55.8	62.2	61.8
Caliper (mm)	0.122	0.139	0.148
Apparent Density (g/cc)	0.459	0.444	0.418
Bulk (cc/g)	2.18	2.25	2.39
Mullen Burs (kPa)	81.1	58.3	33.2
Tensile Strength (kg/m)	143	113.0	67.3
Breaking Length (km)	2.569	1.822	1.089

The percentage loss in strength based upon the above-tabulated results appear below:

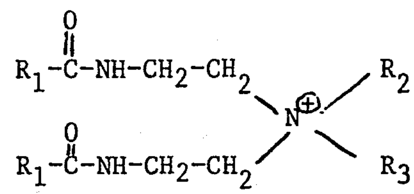
Test	Sample No. (%-loss)	
	SC61-53	SC50-40F
Mullen Burst	28.1	59.1
Tensile Strength	21.0	52.9

The above-tabulated results show that the addition of the alkoxylated fatty acid to the quaternary debonder resulted in a 40% loss in Mullen Burst strength and a 67% loss in Tensile Strength. The dramatic effect of the debonder formulation is demonstrated.

CLAIMS:

1. A debonded cellulose fiber pulp web possessing reduced interfiber bonding and reduced mechanical strength characterized by said web being impregnated with a debonding formulation comprising:

(a) a quaternary ammonium compound having the general formula:

(a) 

where R_1 = C_8-C_{30} aliphatic group,

R_2 =(polyoxy alkylene)hydroxyl alkyl group

R_3= C_1-C_4 alkyl group

X^-= monovalent anion; and

(b) an akoxylated C_8-C_{30} fatty acid or fatty alcohol .

2. The debonded cellulose fiber pulp web of claim 1 which is impregnated with between about 0.1% and 2% of said debonding formulation by weight of said dry pulp solids.

3. The debonded cellulose fiber pulp web of claim 2 which is impregnated with between about 0.2% and 1% of said debonding formulation.

4. The debonded cellulose fiber pulp web of claim 1 wherein for said quaternary ammonium compound (a), R_1 is a C_{12}-C_{18} aliphatic group and R_2 is an ethoxylate, polyethoxylate, propoxylate, or poly-propoxylate residue.

5. The debonded cellulose fiber pulp web of claim 1 wherein said alkoxylated fatty acid or fatty alcohol (b) is an ethoxylated C_{12}-C_{22} fatty acid or fatty alcohol.

6. The debonded cellulose fiber pulp web of claim 5 wherein said fatty acid or fatty alcohol is ethoxylated with between about 2 and 12 moles of ethylene oxide per mole of said fatty acid.

7. The debonded cellulose fiber pulp web of claim 4 wherein said alkoxylated fatty acid or fatty alcohol (b) is an ethoxylated C_{12}-C_{22} fatty acid or fatty alcohol which is ethoxylated with between about 4 and 7 moles of ethylene oxide per mole of said fatty acid or fatty alcohol.

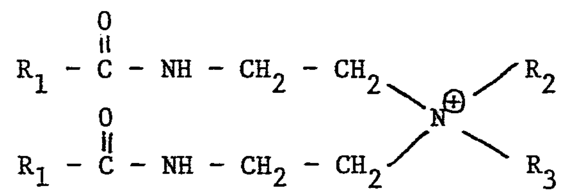
8. The debonded cellulose fiber pulp web of claim 1 wherein

said debonding formulation comprises from between about 10% and 50% by weight of said quaternary ammonium compound (a) and between about 90% and 50% by weight of said alkoxylated fatty acid or fatty alcohol(b).

9. The debonded cellulose fiber pulp web of claim 1 which additionally contains a fluidity-enhancing solvent.

10. The debonded cellulose fiber pulp web of claim 9 wherein said fluidity-enhancing solvent comprises an alkylene glycol.

11. A method for treating cellulose pulp fibers to reduce interfiber bonding and to reduce the mechanical strength of webs formed therefrom, characterized by blending with an aqueous cellulose pulp slurry and debonding formulation comprising:

(a) 

where $R_1 = C_8 - C_{30}$ aliphatic group,

R_2 = (polyoxy alkylene)hydroxyl alkyl group

$R_3 = C_1 - C_4$ alkyl group

X^- = monovalent anion; and

(b) alkoxylated $C_8 - C_{30}$ fatty acid or fatty alcohol .

12. The method of claim 11 wherein said cellulose pulp fibers are blended with between about 0.1% and 2% of said debonding formulation by weight of the dry pulp fibers.

13. The method of claim 12 wherein said cellulose pulp fibers are blended with between about 0.2% and 1% of said debonding formulation.

14. The debonded cellulose fiber pulp web of claim 1 wherein for said quaternary ammonium compound (a), R_1 is a $C_{12}-C_{18}$ aliphatic group and R_2 is an ethoxylate, polyethoxylate, propoxylate, or polypropoxylate residue.

15. The method of claim 11 wherein said blended alkoxylated fatty acid or fatty alcohol is an ethoxylated $C_{12}-C_{22}$ fatty acid or fatty alcohol.

16. The method of claim 15 wherein said fatty acid or fatty alcohol is ethoxylated with between about 2 and 12 moles of ethylene oxide per mole of said fatty acid or fatty alcohol.

17. The method of claim 14 wherein said alkoxylated fatty acid or fatty alcohol is an ethoxylated C_{12}-C_{22} fatty acid or fatty alcohol which is ethoxylated with between about 4 and 7 moles of ethylene oxide per mole of said fatty acid.

18. The method of claim 11 wherein said debonding formulation which is blended with said aqueous cellulose pulp slurry comprises between about 10% and 50% by weight of said quaternary ammonium compound (a) and between about 90% and 50% by weight of said alkoxylated fatty acid or fatty alcohol (b).

19. The method of claim 18 wherein said debonding formulation additionally contains a fluidity-enhancing solvent.

20. The method of claim 19 wherein said fluidity-enhancing solvent is an alkylene glycol.

European Patent Office

EUROPEAN SEARCH REPORT

0116512

Application number

EP 84 63 0017

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. 3)
Y	EP-A-0 049 924 (THE PROCTER & GAMBLE CO.) * Whole document *	1-4,11-14	D 21 H 3/02 D 21 C 9/00 A 61 L 15/00
A		5-9,15-19	
Y	GB-A-1 030 396 (I.C.I. ORGANICS) * Page 1; page 2, lines 46-72; examples 11,14 *	1-4,11-14	
D,A	US-A-4 144 122 (J.G. EMANUELSSON et al.) * Columns 1,2; examples 1-10 *	1-4,9-14,19,20	
A	FR-A-2 431 569 (KENOGARD)		**TECHNICAL FIELDS SEARCHED (Int. Cl. 3)**
A	DE-A-2 254 120 (W. PELZ)		A 61 L C 11 D D 21 C D 21 H
A	US-A-3 677 886 (L.-H. FORSSBLAD et al.)		
A	US-A-4 233 164 (J.E. DAVIS)		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-05-1984	NESTBY K.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document