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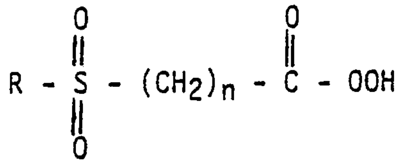
(54) Alkyl sulphonyl peroxycarboxylic acids and bleaching and detergent compositions containing the same.

(57) The present disclosure relates to alkyl sulphonyl peroxycarboxylic acids, processes for preparing such acids, and their use as additives in bleaching, detergent, cleaning and/or disinfecting compositions.

Alkyl sulphonyl peroxycarboxylic acids and bleaching and detergent compositions containing the same

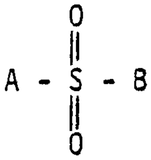
The invention relates to storage-stable bleaching agents of the general structural formula



$$R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-(CH_2)_n-\overset{\overset{O}{\|}}{C}-OOH$$

where R is a linear or branched alkyl group and n is equal to 1 or more. The invention also relates to detergent, bleaching, cleaning and/or disinfecting compositions which incorporate such bleaching agents.

European Patent Application 0 267 175 broadly discloses sulfone peroxycarboxylic acids of the general formula



$$A-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-B$$

wherein A and B are organic moieties and A or B contains at least one C(O) - OOH group. According to European Patent Application 0 267 175, A and/or B may incorporate any of many organic substituents, including alkyl, aralkyl (inclusive of cyclic, straight and branched chain radicals), aryl groups and alkaryl groups. Organic substituents having 1-18 carbon atoms are preferred for A and B. In its examples, European Patent Application 0 267 175 reports the bleaching and stability performance of various sulfone peroxycarboxylic acids, including 3-decylsulfonylperoxypropionic acid.

European Patent Application No. 0 166 571 provides a broad disclosure of peracids which may be used as cleaners and laundry bleaches. In said patent application, peracids of the following general formula are disclosed:

$[RX]_m^{AOOH}$

where R is hydrocarbyl or alkoxylated hydrocarbyl, X is 0, SO_2, $N(R')_2$, $P(R')_2$, $P(R')$—0 or $N(R)$—0 (where R′ is H or alkyl) and A is one of various carbonyl-containing radicals. Only three peracids (in the form of bleach activators) are actually produced as working examples in European Patent Application No. 0 166 571. In those three peracids "X" is always oxygen. The current invention has for its objective to provide particular alkyl sulphonyl peroxycarboxylic acids which have superior stability in their peracid form.

The bleaching agents of the current invention are of the type indicated above and are characterized in that the linear or branched alkyl group R contains 6 to 9 carbon atoms and n is an integer between 1 and 10, inclusive. Preferably, n = 2 or 3. Most preferably, the alkyl group R contains 6 to 9 carbon atoms and n = 2. Specific examples of the alkyl groups of the current invention include n-hexyl, n-heptyl, n-octyl, t-octyl, 2-ethylhexyl, 3,5,5-trimethyl hexyl, n-nonyl and t-nonyl.

The alkyl sulphonyl peroxycarboxylic acids of the current invention may be prepared by reacting a precursor carboxylic acid, such as alkyl sulphonyl carboxylic acid, alkyl mercaptosulphonyl carboxylic acid or alkyl sulphoxyl carboxylic acid, with hydrogen peroxide in an acidic medium. The reaction mixture of carboxylic acid and hydrogen peroxide may be enhanced by the presence of an additional acid, such as methane sulphonic acid or sulphuric acid. The alkyl sulphonyl carboxylic acids and alkyl mercaptocarboxylic acids may be prepared according to L. Rapoport et al., *J. Am. Chem. Soc.*, vol. 69, pages 693-4 (1947). The alkyl mercaptocarboxylic acids may also be prepared by one of the following processes:

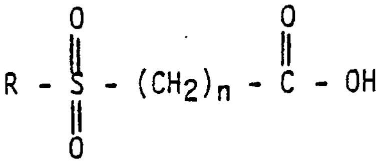
(1) condensing a mercaptan with a haloacid, haloester or halonitrile then hydrolyzing the reaction product;

(2) alkylating a mercaptocarboxylic acid with an alkyl halogenide;

(3) reacting a mercaptocarboxylic acid, ester or nitrile with an alkene then hydrolyzing the reaction product; or

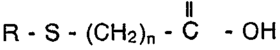
(4) reacting a mercaptan with acrylic acid, acrylic esters or acrylonitrile then hydrolyzing the reaction product.

Specific precursor carboxylic acids which are useful in the processes of the current invention are an alkyl sulphonyl carboxylic acid of the following formula



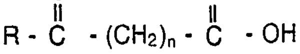
$$R - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - (CH_2)_n - \overset{\overset{O}{\|}}{C} - OH$$

an alkyl mercaptocarboxylic acid of the following formula



$$R - S - (CH_2)_n - \overset{\overset{O}{\|}}{C} - OH$$

or an alkyl sulphoxyl carboxylic acid of the following formula



$$R - \overset{\overset{O}{\|}}{C} - (CH_2)_n - \overset{\overset{O}{\|}}{C} - OH$$

wherein R is a linear or branched alkyl group containing 6 to 9 carbon atoms and n is an integer between 1 and 10, inclusive.

Additionally the alkyl sulphonyl peroxycarboxylic acids of the current invention may also be prepared in situ in a liquor or solution for washing, bleaching, cleaning and/or disinfecting. Such in situ preparation of the compounds of the current invention is carried out in a manner similar to that described in references known in the art which employ bleach activators (for example, U.S. patents 3 163 606 and 4 412 934 and the European patent application 202 698).

As mentioned above, the compound according to the invention is an effective bleaching agent. Therefore the compound may be advantageously employed in bleaching, detergent, cleaning and/or disinfecting compositions. The amount of the current compound which is used in such compositions varies depending on the desired use. Further, it may be desirable to prepare blends or mixes of two or more compounds of the current invention to obtain a combined bleaching agent. For example, some compounds are more effective bleaches for hydrophobic stains while others are more effective for hydrophilic stains. Bleaching agents may also be obtained by mixing or blending one or more compounds of the current invention with other effective bleaches.

Detergent compositions incorporating the bleaching agent of the current invention will also contain a surfactant. Suitable surfactants for use in the present composition are the anionic, non-ionic and amphoteric surface active agents generally employed for this purpose. As examples thereof may be mentioned soaps of synthetic and natural fatty acids, alkyl benzene sulphonates, aliphatic sulphonates, addition products of ethylene oxide to fatty alcohols, ethylene oxide/propylene oxide copolymers and carboxyl group-, sulphate group- or sulphonate group-containing betaines. In addition to the current bleaching agent and at least one surfactant, detergent compositions of the current invention may contain the additives usually employed for detergent compositions, such as sequestering agents, fillers, builders, enzymes, fluorescent and optical brightening or whitening agents, dirt suspending agents, foam suppressors and the like. In actual practice, the detergent composition according to the invention may be in the form varying from powdered to granular and may be prepared by methods known in the art, such as crystallization or spray drying of an aqueous slurry or mechanical mixing of the substances.

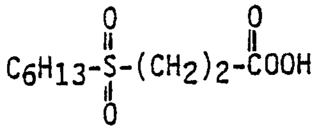
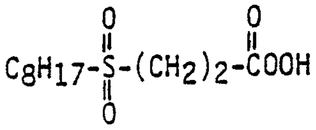
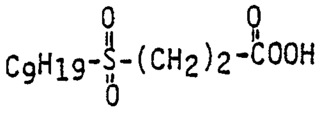
Solid detergent compositions and/or bleach compositions containing alkyl sulphonyl peroxycarboxylic acids may also contain binders to provide mechanical strength and stability. For safety reasons, exotherm control agents may also be used with compositions of the current invention. The alkyl sulphonyl peroxycarboxylic acids of the current invention may also be formulated as liquid suspensions similar to those taught in European patent application 176 124.

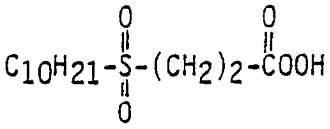
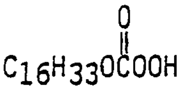
The present examples illustrate the invention.

Example 1

This Example 1 provides a description of the laboratory procedure used to prepare the alkyl sulphonyl peroxycarboxylic acid bleaching agents of the current invention. Table 1 below summarizes the preparation of three representative compounds. To produce the compounds of Table 1, a mixture of 50 ml of methane sulphonic acid ($MeSO_3H$-98%) and 0.075 mole of the precursor alkyl sulphonyl carboxylic acid was prepared for each compound. The precursor alkyl sulphonyl carboxylic acids were n-hexyl sulphonyl propionic acid, n-octyl sulphonylpropionic acid, n-nonyl sulphonyl propionic acid and n-decyl sulphonyl propionic acid for compounds 1, 2, 3 and A, respectively. Compound A is a comparative example since it is disclosed in European Patent Application 0 267 175. Over a period of 30 minutes, 0.225 mole H_2O_2 was added to each constantly stirred mixture of methane sulphonic acid and carboxylic acid. The temperature of the reaction mixture was maintained at 30° C. Stirring was continued for an additional 60 minutes at 30° C. The reaction mixture was poured into 200 ml of ice water. The resulting peracid particles were isolated by filtration (G-3 glasfilter). The obtained wet cake was dissolved in a 1:1 mixture of dichloromethane and ethylacetate then washed with water until the spent wash water had a neutral pH. Each peracid was isolated by removing the solvents in vacuo, producing a white powder. The yield from each reaction was determined by standard iodometric procedures (based on active oxygen). It should be noted that the order in which the alkyl sulphonyl carboxylic acid, an additional acid (such as methane sulphonic acid) and H_2O_2 are combined is not essential to achieving the desired reaction product (alkyl sulphonyl peroxycarboxylic acid). That is, the reaction product is not dependant on the order of mixing. However, the order of mixing for the compounds of this Example 1 was employed for safety reasons.

Table 1

Compound No.	Compound Name	Compound Formula	Yield (%)
1	n-hexyl sulphonyl peroxy propionic acid	 $C_6H_{13}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-(CH_2)_2-\overset{\overset{O}{\|}}{C}OOH$	93.0
2	n-octyl sulphonyl peroxy propionic acid	 $C_8H_{17}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-(CH_2)_2-\overset{\overset{O}{\|}}{C}OOH$	95.7
3	n-nonyl sulphonyl peroxy propionic acid	 $C_9H_{19}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-(CH_2)_2-\overset{\overset{O}{\|}}{C}OOH$	98.0

A	n-decyl sulphonyl peroxy propionic acid	 $C_{10}H_{21}-\overset{\overset{O}{\Vert}}{\underset{\underset{O}{\Vert}}{S}}-(CH_2)_2-\overset{\overset{O}{\Vert}}{C}OOH$	91.0
B	o-cetyl peroxy carb onic acid	 $C_{16}H_{33}O\overset{\overset{O}{\Vert}}{C}OOH$	91.0

Compound Example B is one of the compounds disclosed in European Patent Application 0 166 571 and is thus a comparative example.Compound B was prepared by the following method. To a 0° C mixture of 181.7 g of demineralized water, 0.47 g of the sequestering agent for metallic ions (Dequest® 2060 S (50%)), 170.0 g methanol, 215 mmole NaOH (32.7%), 215 mmole H_2O_2 (69%) and 482.7 g CCl_4 was added under stirring 47.6 mmole cetyl-chloroformate (97.5%) in 54.2 g CCl_4. The addition took place over a 90 minute period. During addition the temperature was maintained at 0° C. Stirring was continued for an additional period of 4 hours at 0° C. The obtained thick slurry was filtered over a G-2 and washed 5 times with demineralized water. The filtering and washing were carried out at 0° C in vacuo (1 mm Hg) providing 12.5 g solid material having an active oxygen content of 4.93% and a yield of 71.1%. A solution of 2.84 g sodium salt of the peracid (active oxygen content = 3.68%) in 140 ml acetic acid was prepared at 20° C. To this solution 100 ml CCl_4 and 350 ml demineralized water were added sequentially. The CCl_4 layer was separated then washed 5 times with 50 ml demineralized water. After drying on $MgSO_4 \cdot 2H_2O$, titration and removing CCl_4 in vacuo, the obtained peroxy carbonic acid was a solid residue having an active oxygen content of 4.29% and a yield of 91% on sodium salt. The structure was confirmed by IR and 1 H NMR spectroscopy.

Example 2

Bleaching agents which have low loss of active oxygen over time are preferred for detergent, bleaching, cleaning and disinfecting compositions. Bleaching agents which have low active oxygen loss are often referred to as "storage stable". The storage stability of the bleaching agents of the current invention were compared to that of a known bleaching additive by storing Compounds 1, 2, A and B at the conditions specified in Tables 2A and 2B. The active oxygen of each compound was determined at designated time intervals by standard iodometric procedures. The results are contained in Tables 2A and 2B. A comparison of Table 2A and Table 2B demonstrates the clear and surprising superiority of the storage stability of the compounds of the current invention. This is true even though the compounds of the current invention were stored at a temperature substantially higher than the storage temperature of Compound A and higher temperatures promote active oxygen loss.

Table 2A

Compound	Storage Temp. (° C)	Initial A.O. (%)	Relative A.O. loss (%)	
			27 days	56 days
1	50	6.59	6.1	23.1
2	50	6.01	6.2	8.7
A	50	5.18	8.1	29.7

Table 2B

Compound	Storage Temp. (°C)	Initial A.O. (%)	Relative A.O. loss (%)		
			13 days	30 days	48 days
B	20	4.14	22.2	36.7	49.3

Example 3

It is also important that bleaching agents retain their storage stability when they are combined in detergent compositions. To demonstrate such stability of the bleaching agents of the current invention, the storage stability of Compound 2 in combination with a standard test detergent ("IEC detergent") was compared with that of the commercially available bleaching agent "DPDA (desensitized) 12%" (12 wt.% diperoxydodecandioic acid and 88 wt.% Na_2SO_4). "DPDA (desensitized) 12%" is hereinafter referred to as "Compound C". The standard detergent was of the following composition:

- 8%	sodium linear alkyl (average $C_{11\frac{1}{2}}$) benzene sulphonate
- 2,9%	ethoxylated (14 EO) tallow alcohol
- 3,5%	sodium soap (13-26% $C_{12\text{-}16}$; 74-78% $C_{18\text{-}22}$)
- 43,7%	sodium triphosphate
- 7,5%	sodium silicate (siO_2 : Na_2O = 3,3 : 1)
- 1,9%	magnesium silicate
- 1,2%	carboxymethyl cellulose
- 0,3%	sodium ethylene diamine tetraacetate
0,3%	optical whitening agent for cotton (stilbene type)
- 21%	sodium sulphate
- 9,7%	water.

Two test samples were prepared by adding 400 mg of Compound 2 and 400 mg of Compound C to two separate 600 mg samples of IEC detergent. The active oxygen content of each sample was determined by standard iodometric procedures then the samples were stored at 40°C for 2 weeks. After 2 weeks Compound 2 retained 95% of its initial active oxygen and Compound C retained only 55% of its initial active oxygen.

Example 4

Two separate groups of laboratory test washings were performed to demonstrate how varying the alkyl chain length of alkyl sulphonyl carboxylic acids affects the laundry bleaching performance of such acids.

In the first group of laboratory test washings, a laboratory Linitest washer was used to examine the bleaching effectiveness of Compounds 1, 2 and A, as defined in Example 1. A control test washing without a bleaching additive of the current invention was also performed. In all four Linitest laboratory test washings, tea and red wine stained fabric swatches (4 grams) were washed in Tide® detergent for 30 minutes in 300 ml water at 40°C.

The detergent concentration was 2.0 g/l. The concentration of the alkyl sulphonyl carboxylic acid (if present) was 20 ppm active oxygen. The bleaching effectiveness was determined with the aid of a reflectometer The reflectometer measures the light reflected in all directions at an angle of 45° when a beam of tristimulus blue light is directed perpendicularly to a piece of cloth. The value obtained from the reflectometer is called "reflectance". A higher reflectance indicates better bleaching action. The reflectance values measured for each of the four Linitest laboratory test washings are reported in Table 3A. Analysis of the data reported in Table 3A indicates that the bleaching performance of Compound 1, 2 and 3 (n-hexyl sulphonyl peroxy propionic acid, n-octyl sulphonyl peroxy priopionic acid and n-nonyl sulphonyl peroxy propionic acid, respectively) are better than, or in the case ofolive oil and soot, substantially equal to, the bleaching performance of Compound A (n-hexyl sulphonyl peroxy propionic acid).

In the second group of laboratory test washings, a miniwasher from ITT was used to examine the bleaching effectiveness of Compounds 1 and 2, as defined in Example 1. The effect of multiple wash cycles was also tested. In each miniwasher test washing, 7 towels, each with 4 swatches of stained fabric, were washed in a standard detergent (defined in Example 3) for 10 minutes (each cycle) in 12 l water at 38° C. The detergent concentration was 1.25 g/l. The concentration of the alkyl sulphonyl carboxylic acid was 6 ppm active oxygen. The bleaching effectiveness was determined by a reflectometer as described above. The reflectance values measured for each miniwasher test are reported in Table 3B. The data in Table 3B demonstrates that Compound 2 is a more effective bleaching agent than Compound 1. (It should be noted that a miniwasher test is more sensitive than a Linitest.) In addition, the data indicata that the superior performance of Compound 2 is more marked for hydrophobic stains (Stains 4 through 7 of Table 3B) than for hydrophobic stains (Stains 1 through 3 of Table 3B).

Table 3A

Stain *	% Reflectance				
	Compound 1 (C_6)	Compound 2 (C_8)	Compound 3 (C_9)	Compound A (C_{10})	No Bleach
1. Tea	55.4	53.4	54.4	51.2	44.8
2. Red Wine	68.2	64.9	61.1	57.4	49.3
3. Berries	67.8	64.8	58.1	52.5	44.8
4. Olive Oil and Soot	24.3	24.6	25.8	26.7	24.2
5. Immedial green	29.1	28.4	28.0	24.7	21.2
6. Chlorophyl	79.0	79.0	79.0	79.0	72.1

* Test swatches were obtained from the following sources:

a. Swatches for stain 2 and 4 were obtained from Eidgen. Materialprufungs und Versuchsanstalt, St. Gallen, Switzerland.

b. Swatch for stain 3 was obtained from the Laundry Research Institute, TNO, Delft, The Netherlands.

c. Swatch for stain 5 was obtained from the Laundry Research Institute, Krefeld, West Germany.

d. Swatch for stains 1 and 6 were prepared by laboratory personnel.

Table 3B

	% Reflectance					
No. Wash Cycles	1		2		3	
Compound	1	2	1	2	1	2
Stain*						
1. Tea	52.4	52.4	57.3	59.1	61.5	62.3
2. Red Wine	60.3	62.2	68.5	68.3	72.0	71.8
3. Berries	54.8	55.2	62.6	63.4	66.3	66.7
4. Raw Cotton (no stain)	69.1	69.6	70.3	70.7	73.1	75.2
5. Olive oil and soot	24.6	27.9	27.8	31.8	29.2	32.7
6. Cocoa	39.1	40.6	41.6	42.6	42.8	43.3
7. Immedial Green	22.1	23.7	24.0	26.6	25.6	28.1

* Test swatches were obtained from the following sources:

a. Swatches for stain 2, 4, 5 and 6 were obtained from Eidgen. Materialprufungs and Versuchsanstalt, St. Gallen, Switzerland.

b. Swatch for stain 3 was obtained from the Laundry Research Institute, TNO, Delft, The Netherlands.

c. Swatch for stain 7 was obtained from the Laundry Research Institute, Krefeld, West Germany.

d. Swatch for stain 1 was prepared by laboratory personnel.

Example 5

This example compares the bleaching performance of a n-hexyl sulphonyl peroxypropionic acid (Compound 1 as defined in Example 1) to the bleaching performance of the highly effective bleaching agent diperoxydodecanedioic acid (DPDA). For a discussion of DPDA as a bleaching agent, see, for example, the article:

"Diperoxydodecanedioic Acid (DPDDA) a New Bleaching Agent for Low-Temperature Laundry Process" by Dr. Peter Kuzel, Dr. Thomas Lieser and Dr. Manfred Dankowski, published in Seifen-Ole-Fette-Wachse, 15, p. 448 (1985).

All tests of this Example 5 were run in a drum-type household Miele® washer in about 20 l tap water (hardness about 1 m mole/l) at 30° C with 125 g standard detergent (defined in Example 3). Each wash load consisted of terry cloth towels and five additional towels, each additional towel containing 4 6x6 cm stained swatches as defined in Table 4. The bleach was rinsed together with the detergent powder into the wash tub. The reflectance of the test swatches was measured by a reflectometer as explained in Example 4. The data in Table 4 demonstrates that the n-hexyl sulphonyl peroxy propionic acid of the current invention provides bleach performance which is better thank or substantially equal to that of DPDA.

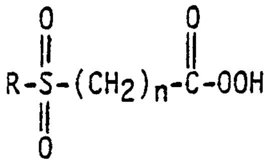
Table 4

	% Reflectance				
Stain*	No Bleach	Compound 1 (6 ppm A.O.)	DPDA (12 ppm A.O.	Compound 1 (12 ppm A.O.)	DPDA (24 ppm A.O.)
1. Tea	52.5	58.3	57.7	62.9	62.6
2. Red Wine	56.9	60.2	61.0	64.8	65.2
3. Berries	46.5	51.7	51.1	58.3	57.9
4. Raw Cotton	62.0	62.6	62.6	63.4	63.6
5. Olive Oil, Soot	25.0	28.8	28.2	32.8	33.1

* Test swatches explained at footnote to Table 3B.

Claims

1. A storage stable bleaching agent of the general structural formula



$$R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-(CH_2)_n-\overset{\overset{O}{\|}}{C}-OOH$$

where R is a linear or branched alkyl group and n is equal to 1 or more characterized in that R contains 6 to 9 carbon atoms and n is an integer between 1 and 10, inclusive.

2. A bleaching agent according to claim 1 characterized in that the alkyl group is n-hexyl, n-octyl or n-nonyl.

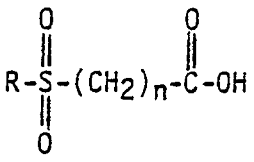
3. A bleaching agent according to any one of the preceding claims characterized in that n = 2 or 3.

4. A combined bleaching agent characterized in that use is made of at least two bleaching agents according to any one of the preceding claims.

5. A detergent, bleaching, cleaning and/or disinfecting composition characterized in that use is made of a bleaching agent according to any one of the preceding claims.

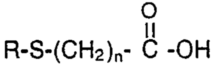
6. A process for preparing a bleaching agent according to any one of the preceding claims 1-4 comprising reacting a precursor carboxylic acid with an effective amount of hydrogen peroxide to form alkyl sulphonyl peroxycarboxylic acid characterized in that the reaction takes place in an acidic medium.

7. The process of claim 7 wherein the precursor carboxylic acid is an alkyl sulphonyl carboxylic acid of the following formula



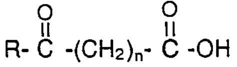
$$R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-(CH_2)_n-\overset{\overset{O}{\|}}{C}-OH$$

an alkyl mercaptocarboxylic acid of the following formula



$$R-S-(CH_2)_n-\overset{\overset{O}{\|}}{C}-OH$$

or an alkyl sulphoxyl carboxylic acid of the following formula



$$R-\overset{\overset{O}{\|}}{C}-(CH_2)_n-\overset{\overset{O}{\|}}{C}-OH$$

or mixtures thereof

wherein R and n are defined as in claim 1.

8. The process of any one of the preceding claims 7 and 8 wherein the precursor carboxylic acid and the hydrogen peroxide are reacted in the presence of at least one additional acid.

9.The process of claim 9 wherein the additional acid is methane sulphonic acid, sulphuric acid or a combination thereof.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 20 0656

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)
D,X	EP-A-0 166 571 (THE PROCTER AND GAMBLE CO.) * Claims * ---	1	C 07 C 179/22 C 11 D 3/39 C 07 C 178/00
D,P X	EP-A-0 267 175 (MONSANTO) * Pages 3-6; claims * -----	1-3,5-9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 179/00 C 07 C 178/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12-06-1989	BONNEVALLE E.I.H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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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

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