

United States Patent [19]

[19]

Staffe et al.

[11] 3,864,396

[45] Feb. 4, 1975

[54] **ACYLATED
PERFLUOROALKANESULPHONAMIDES**

[75] Inventors: **Adolf Staffe, Oplanden; Klaus Gerlach, Cologne, both of Germany**

[73] Assignee: **Bayer Aktiengesellschaft, Leverkusen, Germany**

[22] Filed: **Dec. 8, 1972**

[21] Appl. No.: **313,276**

[30] **Foreign Application Priority Data**

[52] U.S. Cl. 260/556 F, 252/8.75, 260/465.5 R,
260/543 R, 260/543 F, 260/553 R, 260/553
A, 260/556 A, 260/583 P
[51] Int. Cl. C07c 143/74
[58] Field of Search..... 260/556 F, 465.5 R, 553 R,
260/553 A

[56] References Cited

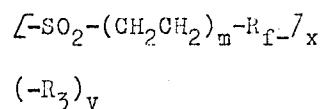
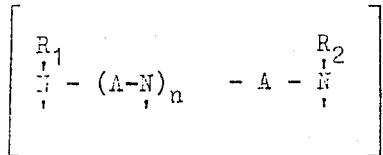
UNITED STATES PATENTS

2,759,019 8/1956 Brown et al. 260/556 F
2,803,656 8/1957 Ahlbrecht et al. 260/556 F

*Primary Examiner—Henry R. Jiles
Assistant Examiner—S. D. Winters
Attorney, Agent, or Firm—Plumley & Tyner*

[57] ABSTRACT

Perfluoroalkanesulphonamides of the formula

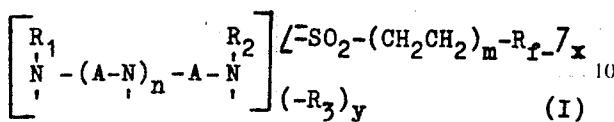


in which A, R₁, R₂, R₃, R_f, m, n, x and y have the meaning given in the disclosure, and a process for their manufacture. The perfluoroalkanesulfonamides are excellent oleophobic agents.

7 Claims, No Drawings

ACYLATED
PERFLUOROALKANESULPHONAMIDES

The invention relates to perfluoroalkanesulphonamides; more particularly it concerns perfluoroalkanesulphonamides of the formula 5



in which

R_1 and R_2 independently of one another represent hydrogen or an optionally substituted alkyl group, A represents an alkylene group which is optionally interrupted by oxygen atoms, preferably a C_2-C_3 -alkylene group,

n denotes a number from 1 to 3,

20

x denotes a number from 2 to $(n+1)$ and y denotes a number from 1 to n ,

R_f represents a perfluorobutyl radical,

m is 1 or preferably 0 and

R_3 is hydrogen or an acyl radical derived from carboxylic acid, oxalic acid or from carboxylic acids or an optionally substituted carbonamide group,

25

with the proviso that R_1 and R_2 only represents an optionally substituted alkyl group if the nitrogen atom to 30 which the two radicals are bonded is an amine nitrogen atom or a sulphonamide nitrogen atom; the invention further relates to a process for the manufacture of the perfluoroalkanesulphonamides of the formula (I) and to their use as oleophobic agents.

35

Possible alkylene groups A are above all alkylene radicals with 2 to 10, preferably with 2 or 3, C atoms, for example the ethylene, ethylidene, propylene-(1,3), butylene-(1,4), hexylene-(1,6) and 4-oxaheptylene-40 (1,7) group.

40

Examples which may be mentioned of optionally substituted alkyl groups which R_1 and R_2 can be are: lower alkyl radicals, for example C_1-C_4 -alkyl radicals, such as the methyl, ethyl, n-propyl, n-butyl and sec.-butyl radical, and lower alkyl radicals substituted by nitrile or lower alkoxy groups, such as the 2-methoxyethyl, 3-methoxypropyl, 2-ethoxyethyl, 3-ethoxypropyl and 2-cyanoethyl radical.

45

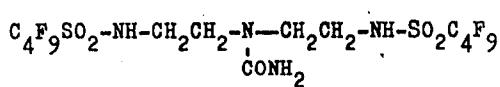
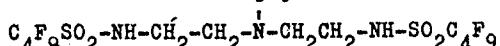
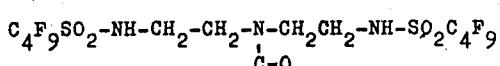
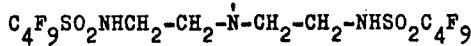
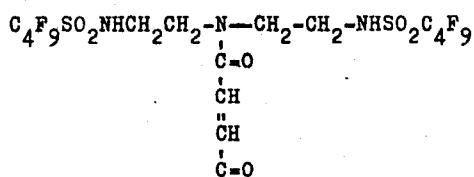
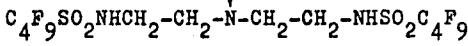
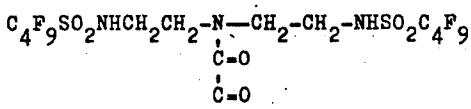
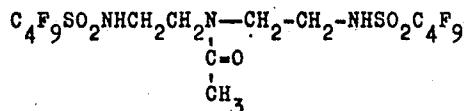
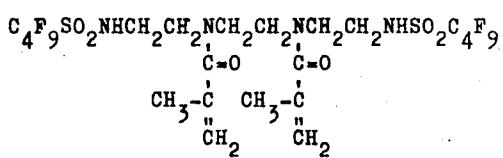
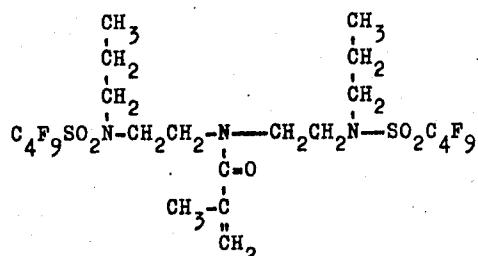
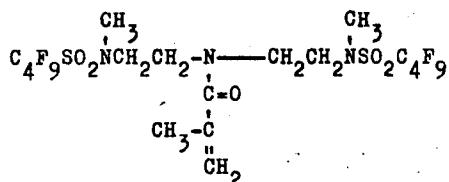
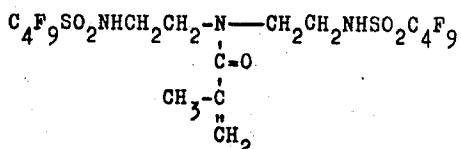
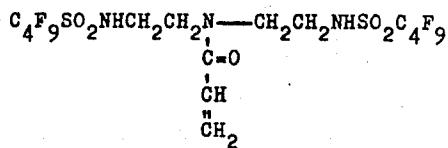
Examples of carboxylic acids from which R_3 is derived as an acyl radical are both aromatic and saturated or unsaturated aliphatic monocarboxylic or dicarboxylic acids. As aromatic carboxylic acids, benzoic acid may especially be mentioned, and as saturated or unsaturated aliphatic carboxylic acids lower monocarboxylic acids may above all be mentioned, such as acetic acid, propionic acid, butyric acid, acrylic acid and methacrylic acid and also lower dicarboxylic acids, such as succinic acid, adipic acid and maleic acid.

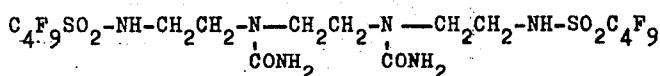
50

As optionally substituted carbonamide groups which R_3 can be there may be mentioned carbonamide groups substituted by C_1-C_6 -alkyl, cyclohexyl or aryl groups, such as the methyl-, methoxymethyl-, ethyl-, cyclohexyl-, phenyl- and tolyl-carbonamide group.

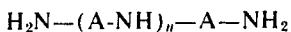
60

As examples of representatives of the perfluoroalkanesulphonamides of the formula (I), according to the invention, there may be mentioned:





The perfluoroalkanesulphonamides of the formula (I), according to the invention, are obtainable in various ways; preferably, they are obtained by reacting polyamines of the formula



(II)

in which

A and n have the meaning indicated under the formula (I)

with perfluoroalkanesulphonyl halides of the formula



(III)

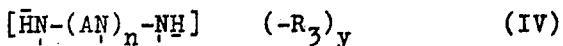
in which

R_f and m have the meaning indicated under the formula (I)

and in which

X represents chlorine or preferably fluorine, and optionally acylating the resulting poly-perfluoroalkane-sulphonyl-polyamines in a manner which is in itself known and/or alkylating them in a manner which is in itself known.

Another possible method of manufacture consists of first acylating the polyamines of the formula (II) in a manner which is in itself known and to react the acylated polyamines of the formula



in which

n and y have the meaning indicated under the formula (I)

with perfluoroalkanesulphonyl halides of the formula (III), in the manner described for the polyamines.

The reaction of the polyamines (II) with the perfluoroalkanesulphonyl halides (III) is carried out at temperatures of 0° to 150°C, preferably 40° to 90°C, in the presence of acid-binding agents, such as inorganic bases, for example potassium carbonate, or organic bases, for example tertiary amines, such as triethylamine or pyridine, or alcoholates, such as sodium methylate, optionally in organic solvents which are inert under the reaction conditions. The molar ratio of polyamine to be reacted and perfluoroalkanesulphonyl halide is so chosen that 2 to (n+1) mols of perfluoroalkanesulphonyl halide are available per 1 mol of polyamine.

The poly-perfluoroalkanesulphonyl-polyamines thus obtained can subsequently be acylated and/or alkylated in a manner which is in itself known.

To introduce the acyl and carbonamide groups the poly-perfluoroalkanesulphonyl-polyamines are reacted in a manner which is in itself known, at temperatures of 0° to 100°C, preferably at 30° to 60°C, optionally in solvents which are inert under the reaction conditions, such as pyridine, benzene, toluene or chlorobenzene, with compounds which react with basic nitrogen atoms to form amides, such as acyl halides, for example ben-

zoyl chloride, acetyl chloride, propionyl chloride, butyryl chloride, acrylic acid chloride, methacrylic acid chloride, chloroformic acid methyl ester or chloroformic acid ethyl ester; acid anhydrides, for example acetic anhydride, succinic anhydride and maleic anhydride; carboxylic acid esters, for example acetic acid methyl ester, propionic acid methyl ester and benzoic acid methyl ester; isocyanates, for example methylisocyanate, methoxymethylisocyanate, ethylisocyanate, cyclohexylisocyanate, phenylisocyanate and tolylisocyanate; and inorganic cyanates, for example potassium cyanate.

To introduce the alkyl groups, the optionally acylated poly-perfluoroalkanesulphonyl-polyamines are converted, in a manner which is in itself known, into the alkali compounds of the sulphonamides, for example by reaction of the sulphonamides with sodium methylate in absolute methanol, and the alkali compounds are reacted, optionally in a solvent which is inert under the reaction conditions, with alkyl halides of the formula RX₁ and/or RX₂.

Instead of starting from polyamines of the formula (II) it is also possible, in manufacturing the compounds of the formula (I) according to the invention, to start from diamines containing cyanoalkyl groups, for example N-cyanoethylmethylenediamine, to react these with perfluoroalkanesulphonyl halides in the manner described above for the polyamines (II), and to reduce the resulting bis-perfluoroalkanesulphonylcyanooalkylamines to the corresponding bis-perfluoroalkanesulphonyl-aminoalkyl-amines. The amines thus obtainable can optionally subsequently be further acylated and/or alkylated as described.

40 The compounds according to the invention, of the formula (I) are valuable agents for the oleophobic finishing of materials made of paper, wood, textiles and yarns.

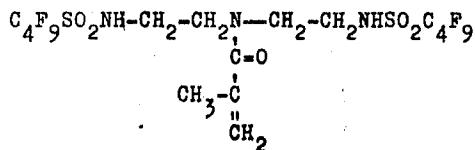
45 It should be emphasised that an excellent oleophobic effect is achieved with the perfluorobutyl group containing sulphonamides of formula (I). This is surprising since hitherto the opinion was held amongst experts (see Textilveredlung 2 / 1967 / page 463) that for oleophobic agents based on perfluoroalkanesulphonamides 50 the chain length of the perfluoroalkyl radical had to be 6 to 8 C atoms.

EXAMPLE 1

55 604 g (2 mols) of perfluoro-n-butanesulphonic acid fluoride are added dropwise, at a temperature of 89°C, to a mixture of 103 g (1 mol) of diethylenetriamine, 505 g (5 mols) of triethylamine and 67.5 g (0.5 mol) of N-dimethylbenzylamine at such speed that the temperature of the reaction mixture does not drop below 80°C. To complete the reaction, the reaction mixture is stirred for 5 hours at 80°C. After distilling off the triethylamine, the residue is dissolved in 550 ml of pyridine. 104 g (1 mol) of methacrylic acid chloride are slowly added dropwise to this solution at 35 to 45°C. 60 The reaction mixture is stirred for a further 6 hours. The bulk of the pyridine is then distilled off under reduced pressure and the residue in the flask is poured

into 1,000 ml of water. The reaction product which has precipitated is filtered off and washed with water until it reacts neutral.

The N,N-Bis-(2-perfluorobutanesulphonylaminoethyl)-methacrylic acid amide



(molecular weight 735) precipitates in the form of a yellowish brown amorphous powder in a yield of 647 g (= 88% of theory).

EXAMPLE 2

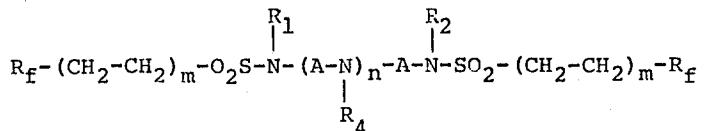
604 g (2 mols) of perfluoro-n-butanesulphonic acid fluoride are slowly added dropwise at a temperature of 89°C to a mixture of 146 g (1 mol) of triethylene-tetramine and 606 g (6 mols) of triethylamine. To complete the reaction, the reaction mixture is stirred for a further 5 hours at 85°C. After distilling off the triethylamine, the residue is dissolved in 600 ml of pyridine. 208 g (2 mols) of methacrylic acid chloride are slowly added dropwise to the solution at 40° to 50°C. The reaction mixture is stirred for a further 6 hours at room temperature. The bulk of the pyridine is then distilled off under reduced pressure and the residue in the flask

perfluorobutanesulphonylaminoethyl)-methacrylic acid amide described in Example 1, in acetone, squeezed out to a weight increase of 50% and dried for 10 minutes at 100°C. This fabric (deposit of oleophobic agent: 0.5 per cent by weight) receives a rating of 100 to 110 in the 3M test.

The oleophobic effect of the fabric, paper and wood products described was assessed in accordance with the socalled "3M oil repellency test" (Crajeck, Petersen, 10 Textile Research Journal 32, page 320 to 331 (1960) with heptane-paraffin oil mixtures. In the assessment, 150 denotes the best achievable rating and 50 the worst rating. The individual samples were assessed immediately after drying.

We claim:

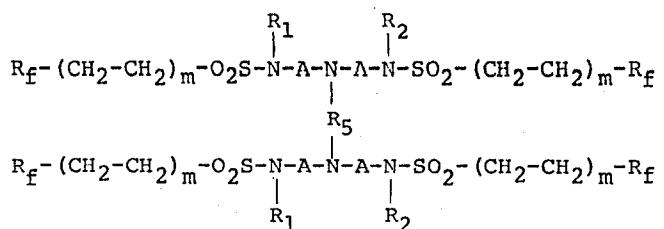
1. Perfluoroalkanesulphonamide of the formula



in which

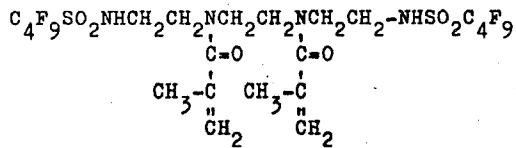
25 R_1 and R_2 independently of one another are hydrogen; $\text{C}_1\text{--C}_4$ -alkyl; or $\text{C}_1\text{--C}_4$ -alkyl substituted by nitrile or lower alkoxy; A is $\text{C}_2\text{--C}_{10}$ -alkylene or $\text{C}_2\text{--C}_{10}$ -alkylene interrupted by oxygen; n is a number from 1 to 3; R_f is perfluorinated butyl; m is 1 or 0; and R_4 is hydrogen; benzoyl; acetyl; propionyl; butyryl; acryl; methacryl; carbonamide; or carbonamide substituted with $\text{C}_1\text{--C}_6$ -alkyl, cyclohexyl, methoxymethyl, phenyl or tolyl.

2. Perfluoroalkanesulfonamide of the formula



is poured into 1,000 ml of water. The reaction product which precipitates is filtered off and washed with water until it reacts neutral.

The N,N'-bis-(2-perfluorobutanesulphonylaminoethyl)-N,N'-bis-methacryloyl-ethylenediamine



(molecular weight 846) is obtained in the form of a brownish amorphous powder in a yield of 778 g (= 92% of theory).

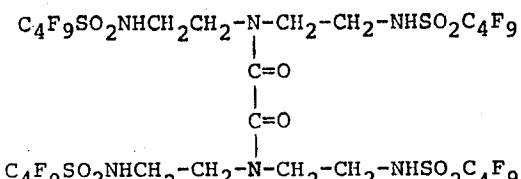
EXAMPLE 3

Cotton fabric was impregnated with a 1% strength solution of the N,N-bis-(2-

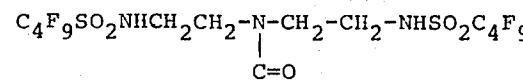
50 in which

R_5 is carbonyl, oxalyl, succinyl, adipyl, or maleyl; R_1 and R_2 independently of one another are hydrogen; $\text{C}_1\text{--C}_4$ -alkyl; or $\text{C}_1\text{--C}_4$ alkyl substituted by nitrile or lower alkoxy; A is $\text{C}_2\text{--C}_{10}$ -alkylene or $\text{C}_2\text{--C}_{10}$ alkylene interrupted by oxygen; R_5 is perfluorinated butyl; and m is 1 or 0.

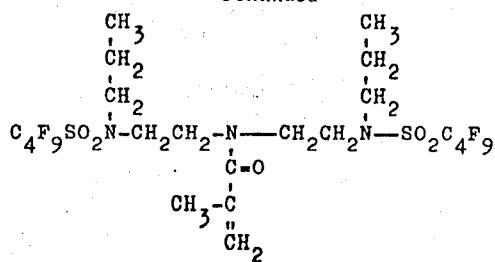
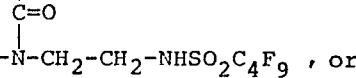
55 3. Perfluoroalkanesulfonamide of claim 2 having the formula



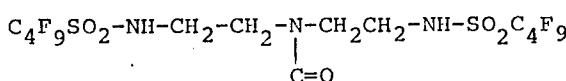
-Continued



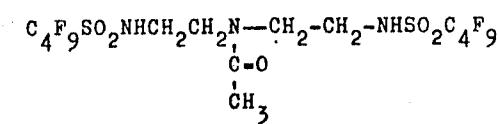
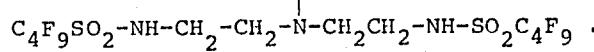
5



10



20

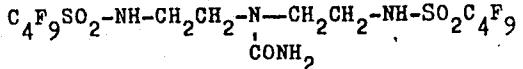


25

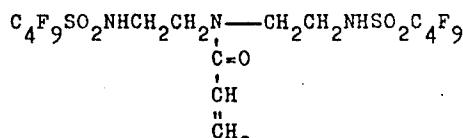
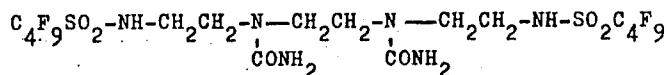
4. Perfluoroalkanesulphonamide of claim 1 in which *m* is 0; and *A* is $\text{C}_2\text{--C}_3\text{-alkylene}$.

5. Perfluoroalkanesulphonamide of claim 1 selected from the group consisting of

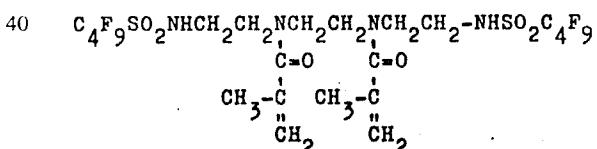
30



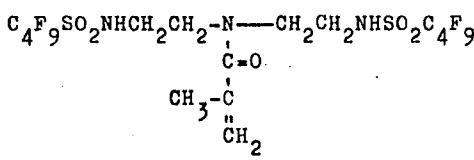
and



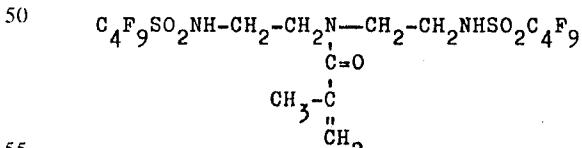
6. Perfluoroalkanesulphonamide of claim 1 having the formula



45



7. Perfluoroalkanesulphonamide of claim 1 having the formula



55

* * * * *

60

65