

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 280 115
A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **88101967.3**

(51) Int. Cl. 4: **D21H 3/02**

(22) Date of filing: **10.02.88**

(30) Priority: **12.02.87 JP 30003/87**

(43) Date of publication of application:
31.08.88 Bulletin 88/35

(84) Designated Contracting States:
DE FR GB

(71) Applicant: **DAIKIN INDUSTRIES, LIMITED**
Umeda Center Building 4-12 Nakazaki-nishi
2-chome Kita-ku
Osaka 530(JP)

(72) Inventor: **Aoyama, Hirokazu**
28-1-707, Nyoze-cho
Takatsuki-shi Osaka-fu(JP)
Inventor: **Amimoto, Yoshio**
2-15-9, Daizohji
Takatsuki-shi Osaka-fu(JP)

(74) Representative: **Hansen, Bernd, Dr.rer.nat. et**
al
Hoffmann, Eitle & Partner Patentanwälte
Arabellastrasse 4
D-8000 München 81(DE)

(54) **Oil proof composition for paper.**

(57) An oil proof composition for paper which comprises at least one salt selected from the group consisting of fluoroalkyl phosphate salts, N-alkyl fluoroalkanesulfonamidoalkyl phosphate salts and fluoroalkenyloxyaralkyl phosphonate salts and at least one anionic surfactant, which can impart not only oil resistance but also a sizing effect and does not precipitate when diluted with hard water or stirred at a high revolution rate.

EP 0 280 115 A1

OIL PROOF COMPOSITION FOR PAPER

BACKGROUND OF THE INVENTIONField of the Invention

5

The present invention relates to an oil proof composition for paper. More particularly, it relates to a composition for imparting oil resistance to paper which comprises a salt of fluorophosphate or a salt of fluorophosphonate and at least one anionic surfactant.

10

Description of the Prior Arts

As oil proof agents for paper, namely sizing agents added to the paper in order to render the sheet more resistant to penetration of oils, salts of fluoroalkyl phosphate or salts of N-alkyl fluoroalkanesulfonylamidoalkyl phosphate are known. Such conventional oil proof agents are applied to paper either by internal addition (internal sizing) which comprises dissolving or dispersing the agent in a pulp suspension or slurry for paper making, or by external addition (surface sizing) which comprises dipping a sheet of paper in an aqueous solution or dispersion of the agent or brushing over the sheet with the solution or dispersion to coat the surface of paper with the agent. In either of these additions, when water has too high hardness, the oil proof agent can be dissolved in a small amount of hard water. However, when the agent is added to a large amount of hard water or the aqueous solution of the agent is diluted with a large amount of hard water, the salt of fluoroalkyl phosphate or the salt of N-alkyl fluoroalkanesulfonylamidoalkyl phosphate is precipitated, which results in decrease of sizing effect or deterioration of oil resistance of processed paper. When other finishing agents such as aluminum sulfate is used, the same drawback arises as when hard water is used.

A salt of fluoroalkenyloxyaralkyl phosphonate may be used as an oil proof agent for paper. But, it has the same drawback as the salt of fluoroalkyl phosphat when it is used in hard water.

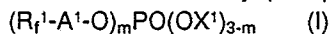
30 SUMMARY OF THE INVENTION

An object of the present invention is to provide an oil proof composition for paper which is not precipitated in hard water and can impart good oil resistance to paper.

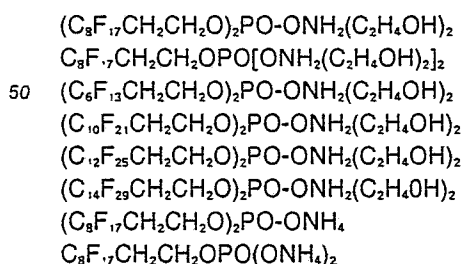
According to the present invention, this and other objects are achieved by an oil proof composition for paper which comprises at least one salt selected from the group consisting of fluoroalkyl phosphate salts, N-alkyl fluoroalkanesulfonylamidoalkyl phosphate salts and fluoroalkenyloxyaralkyl phosphonate salts and at least one anionic surfactant.

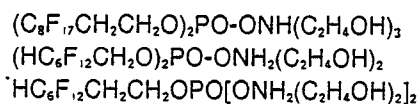
40 DETAILED DESCRIPTION OF THE INVENTION

The salt of fluoroalkyl phosphate may be a salt of the formula:

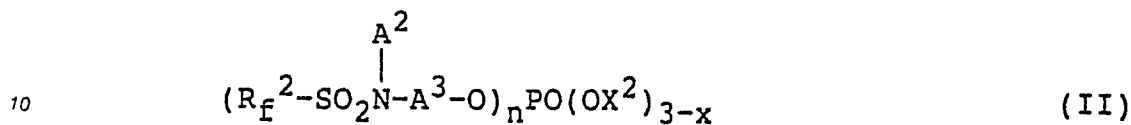


wherein R_1^1 is each a C_5-C_{21} perfluoroalkyl or ω -hydroperfluoroalkyl group, A^1 is each a C_1-C_{10} alkylene group, X^1 is an alkali metal or an ammonium group which may be substituted by a C_1-C_{10} alkyl or hydroxyalkyl group, and m is 1 or 2. Preferred salts (I) are

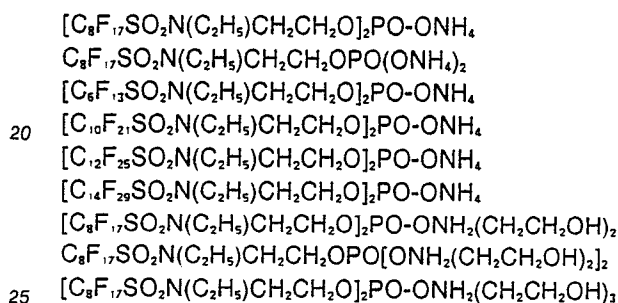




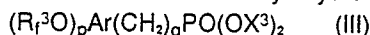
5 The salt of N-alkyl fluoroalkanesulfonamidoalkyl phosphate may be a salt of the formula:



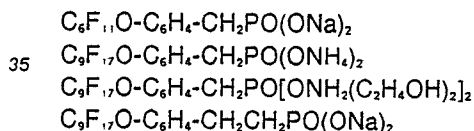
wherein R_f^2 is each a C_5 - C_{21} perfluoroalkyl group, A^2 is each a C_1 - C_{10} alkyl group, A^3 is each a C_1 - C_{10} alkylene group, X^2 is an alkali metal or or an ammonium group which may be substituted by a C_1 - C_{10} alkyl or hydroxyalkyl group, and n is 1 or 2. Preferred salts (II) are



The salt of fluoroalkenyloxyaralkyl phosphonate may be a salt of the formula:



wherein R_f^3 is each a C_6 - C_{12} perfluoroalkenyl group, p is 1, 2 or 3 and Ar is an aromatic group which may have a substituent (e.g. phenyl, naphthyl, or alkyl-, acyl-, alkoxy- or halogen-substituted phenyl or naphthyl), q is 1 or 2 and X^3 is an alkali metal or an ammonium group which may be substituted by a C_1 - C_{10} alkyl or hydroxyalkyl group. Preferred salts (III) are



The above salt of phosphate or phosphonate may be prepared by neutralizing at least one partial ester selected from the group consisting of fluoroalkyl partial esters of phosphoric acid, N-alkyl fluoroalkanesulfonamidoalkyl partial esters of phosphoric acid and fluoroalkenyloxyaralkyl partial esters of phosphonic acid with a base (e.g. hydroxides of alkali metals, amines, etc.) according to a conventional method.

The anionic surfactant is preferably a hydrocarbon type anionic surfactant. Examples of the anionic surfactant are C_5 - C_{15} alkylbenzenesulfonic acids, C_5 - C_{15} alkylbenzenesulfonate salts, di- C_5 - C_{15} alkyl sulfosuccinate salts, C_9 - C_{21} alkyl sulfate salts, C_{10} - C_{20} alkylsulfonate salts, C_7 - C_{15} alkylnaphthalenesulfonate salts, mono- or di- C_9 - C_{21} alkyl phosphate salts, salts of C_9 - C_{25} fatty acids and the like. The salt may be a sodium, potassium, ammonium, mono-, di- or tri- C_1 - C_5 alkyl or hydroxyalkylammonium salt.

The amount of anionic surfactant is from 1 to 15 % by weight based on the weight of phosphate or phosphonate which is converted to the weight of corresponding partial ester.

The oil proof composition of the present invention may be used together with other processing agents such as a bonding agent such as Sumilets resin FC-50L and Sumilets resin 675 (both available from Sumitomo Chemical Co., Ltd.). The amount of bonding agent is from 0.5 to 3 times by weight based on the weight of oil proof composition (the weight of the salt of fluorophosphate and/or fluorophosphonate being converted to a weight of corresponding partial ester).

The oil resistant imparting composition is easily prepared by mixing the salt of phosphate or phosphonate and the anionic surfactant.

Oil resistant imparting composition of the present invention is not precipitated when diluted with comparatively hard water or water containing aluminum sulfate, or when stirred vigorously. Even when the

oil proof composition is added to paper by the internal addition, paper has good properties such as sizing degree in addition to oil resistance.

The present invention will be illustrated by following examples, in which "%" is by weight unless otherwise indicated.

Example 1

Preparation Example

In a 4 liter round flask equipped with a stirrer, $\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ ($n=2$, 1 % by mole; $n=3$, 55 % by mole; $n=4$, 26 % by mole; $n=5$, 12 % by mole; $n=6$, 5 % by mole; $n=7$, 1 % by mole) (300 g) and 85 % phosphoric acid (6.4 g) were charged, and phosphorus oxychloride (33.8 g) was added at a temperature of 80 to 85°C with stirring over 30 minutes. After purging hydrogen chloride gas under reduced pressure, water (28 g) was added and stirred at a temperature of 95 to 100°C for 1 hour. Thereafter, the mixture was cooled to 85°C and isopropanol (66 g) was added to prepare a phosphate ester stock solution having the following composition:

$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$	0.75 %
$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OPO}(\text{OH})_2$	8.45 %
$[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{O}]_2\text{POOH}$	53.24 %
$[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{O}]_3\text{PO}$	15.89 %
Water	3.82 %
Isopropanol	17.85 %

Example 1

In a 4 liter round flask equipped with a stirrer, the phosphate ester stock solution prepared in Preparation Example (400 g) was charged followed by addition of diethanolamine (110 g) at a temperature of 70 to 75°C. Then, sodium salt of dodecyl benzenesulfonate (16 g, 6.5 % per weight of the phosphate salt) and warm water (50 g) were added followed by addition of warm water (1,500 g) to give an emulsion of oil proof agent (pH 10) having the following composition:

$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$	3.0 g
$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OPO}(\text{OH})_2$	246.7 g
$[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{O}]_2\text{POOH}$	(11.9 %)
$[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{O}]_3\text{PO}$	63.6 g
Diethanolamine	110 g (5.3 %)
Na salt of dodecyl benzenesulfonate	16 g (0.8 %)
Isopropanol	71.4 g (3.4 %)
Water	1,565.3 g (75.4 %)

Example 2

In the same manner as in Example 1 but using 5.4 g (2.2 % per weight of the phosphate) of sodium salt of dodecyl benzenesulfonate, an emulsion of oil proof agent (pH 10) was prepared.

Example 3

To the emulsion of oil proof agent prepared in Example 1, hydrochloric acid was added to give an emulsion of oil proof agent having pH of 7.

Example 4

In the same manner as in Example 1 but using 16 g of sodium salt of dioctyl sulfosuccinate in place of sodium salt of dodecyl benzenesulfonate, an emulsion of oil proof agent (pH 10) was prepared.

Example 5

In the same manner as in Example 1 but using 28 % ammonia water (110 g) in place of diethanolamine, an emulsion of oil proof agent (pH 10) was prepared.

Example 6

In the same manner as in Example 5 but using 16 g of sodium dioctylsulfosuccinate in place of sodium salt of dodecyl benzenesulfonate, an emulsion of oil proof agent (pH 10) was prepared.

Example 7

In the same manner as in Example 6 but using 11.2 g of sodium dioctylsulfosuccinate (4.5 % per weight of the phosphate), an emulsion of oil proof agent (pH 10) was prepared.

Examples 8 and 9

To the emulsion of oil proof agent obtained in Example 6, hydrochloric acid was added to give an emulsion of oil proof agent having pH of 9 (Example 8) or pH of 7 (Example 9).

Comparative Example 1

In the same manner as in Example 1 but using no surfactant, an emulsion of oil proof agent was prepared.

Comparative Example 2

In the same manner as in Example 5 but using no surfactant, an emulsion of oil proof agent was prepared.

The compositions and pH values of the oil proof compositions prepared in Examples and Comparative Examples are summarized in Table 1.

Table 1

Example No.	Base component of phosphate	Anionic surfactant (content)	pH of the emulsion
1	Diethanolamine	Na salt of dodecyl benzenesulfonate (6.5 %)	10
2	↑	↑ (2.2 %)	10
3	↑	↑ (6.5 %)	7
4	↑	Na salt of dioctyl sulfosuccinate (6.5 %)	10
5	NH ₃	Na salt of dodecyl benzenesulfonate (6.5 %)	10
6	↑	Na salt of dioctyl sulfosuccinate (6.5 %)	10
7	↑	↑ (4.5 %)	10
8	↑	↑ (6.5 %)	9
9	↑	↑ (6.5 %)	7
Com.1	Diethanolamine	----	9
Com.2	NH ₃	----	7

Experiment 1

Dilution stability of the emulsion of oil proof agent prepared in Example 2 or Comparative Example 1 was examined.

The emulsion was diluted with water having various hardness to adjust the concentration of the oil proof agent to 1 %. Then, one portion of the diluted emulsion was stirred at 3,000 ppm for 3 minutes while another portion was not stirred. Then, both were kept standing for one day and a precipitated amount per 10 ml was measured. The results are shown in Table 2.

Table 2

	Hardness of water (CaCO ₃)	Precipitated amount (ml)	
		Stirring	No stirring
Example 2	0	0	0.01
	100	0.01	0.10
	200	0.01	0.12
	300	0.01	0.20
Comparative Example 1	0	0	0.50
	100	0.02	1.92
	200	0.03	2.11

Experiment 2

Stability against aluminum sulfate of the same emulsions of oil proof agents as used in Experiment 1 was examined.

To 100 ml of the emulsion containing 0.5 % of the oil proof agent, 0.2 ml or 0.5 ml of a 1 % aqueous solution of aluminum sulfate was dropwise added and kept standing at room temperature for 1 hour. Just after the addition of aluminum sulfate and after kept standing for 1 hour, a precipitation state was observed and evaluated according to the following criteria:

O: No precipitate

Δ: Few precipitates

X: A few precipitates

XX: Many precipitates

The results are shown in Table 3.

Table 3

	0.2 ml addition		0.5 ml addition	
	Just after addition	After 1 hour	Just after addition	After 1 hour
Example 2	O	O	Δ	Δ
Comparative Example 1	Δ	X	X	XX

Experiment 3

Mechanical stability of the emulsion of oil proof agent was evaluated.

Each of the emulsions of oil proof agents prepared in Examples 1-9 and Comparative Examples 1 and 2 was stirred at 3,000 rpm for 3 minutes and condition of the emulsion was observed and evaluated according to the following criteria:

OO: No precipitate

O: Few precipitates

Δ: A few precipitates

X: Many precipitates

The results are shown in Table 4.

Table 4

Exam- ple No.	Mecha- nical Stabi- lity	Sumilets resin FC-50L		Sumilets resin 675	
		Oil resistance	Sizing degree	Oil resistance	Sizing degree
1	O	12	4.1	12	26.4
2	O	12.5	4.9	12.5	25.8
3	O	12	3.6	11.5	20.9
4	Δ	13	3.9	11.5	18.4
5	O	13 ⁺	5.1	11	19.2
6	OO	13 ⁺	3.6	11 ⁺	19.1
7	OO	14	3.3	11 ⁺	20.2
8	OO	14	4.4	11.5	21.4
9	OO	14	3.1	10	12.9
Com. 1	X	12	2.3	11.5	17.9
Com. 2	X	13	3.0	11.5	18.6

Experiment 4

A sizing effect of each of the emulsions of oil proof agents prepared in Examples 1-9 and Comparative Examples 1 and 2 was evaluated. By using, as a bonding agent, Sumilets resin FC-50L (0.2 % per weight of pulp) or Sumilets 675 (0.3 % per weight of pulp), the oil proof composition (0.35 % of solid materials per weight of pulp) was added to paper by the internal addition method.

The sizing degree was measured as follows:

From a sheet of paper containing the oil proof composition, a square piece of paper (50 mm × 50 mm) was cut out and its peripheral parts were folded upwardly along lines about 1 cm inside from and in parallel with the four edge lines to make a small box. As soon as the box was placed on a surface of a 2 % aqueous solution of ammonium rhodanate in a petri dish kept at 20±1°C, a drop of a 1 % aqueous solution of ferric chloride kept at the same temperature was added in the box. Then, a period of time till three red spots appeared on the bottom of the paper box was measured.

The sizing effect was expressed in terms of such period of time. The results are shown in Table 4.

Experiment 5

Oil resistance of the paper as prepared in Experiment 4 was evaluated as follows:

Castor oil (chemically pure (c.p.) grade), toluene (c.p. grade) and heptane (c.p. grade) were mixed in a ratio shown in Table 5 to prepare mixed solvent Nos. 1 to 16. Then, each mixed solvent was dropped on a sheet of paper placed on a clean flat surface from a height of about 2.5 cm above the sheet of paper. After 15 seconds from the completion of dropping of the mixed solvent, conditions of the paper sheet where the mixed solvent was dropped were observed. When any black spot was formed, the oil resistance was evaluated as "unacceptable" irrespective of the area of the spot, while no spot was formed, the oil resistance was evaluated as "acceptable". The oil resistance was expressed in terms of the maximum number of mixed solvent for which the oil resistance was acceptable. The larger the number of mixed solvent, the better the oil resistance of paper. The results are also shown in Table 4 above.

Table 5

Mixed solvent No.	Castor oil (ml)	Toluene (ml)	Heptane (ml)
1	200	0	0
2	180	10	10
3	160	20	20
4	140	30	30
5	120	40	40
6	100	50	50
7	80	60	60
8	60	70	70
9	40	80	80
10	20	90	90
11	0	100	100
12	0	90	110
13	0	70	130
14	0	50	150
15	0	30	170
16	0	0	200

Example 10

In a 4 liter round flask equipped with a stirrer, the phosphate ester stock solution prepared in Preparation Example (400 g) was charged followed by addition of diethanolamine (110 g) at a temperature of 70 to 75°C. Then, sodium salt of dodecyl benzenesulfonate (7.4 g, 3.0 % per weight of the phosphate salt) and warm water (50 g) were added followed by addition of warm water (1,500 g) to give an emulsion of oil proof agent (pH 10) having the following composition:

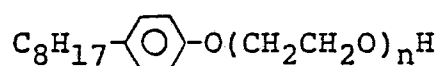
10	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$	3.0 g
	$\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OPO}(\text{OH})_2$	246.7 g
15	$[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{O}]_2\text{POOH}$	(11.9 %)
	$[\text{CF}_3\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{O}]_3\text{PO}$	63.6 g
	Diethanolamine	110 g (5.3 %)
20	Na salt of dodecyl benzenesulfonate	7.4 g (0.4 %)
	Isopropanol	71.4 g (3.5 %)
25	Water	1,565.3 g (75.7 %)

30

Comparative Example 3

In the same manner as in Example 10 but using Nonion HS-220 (a nonionic surfactant,

35



40

in which an average of n is 20 manufactured by Nippon Oil and Fat Co., Ltd.) (7.4 g) in place of the sodium salt of dodecyl benzenesulfonate, an emulsion of oil proof agent was prepared.

Experiment 6

45

Stability against dilution with hard water of the emulsion of oil proof agent prepared in Example 10 or Comparative Example 3 was examined.

50

The emulsion was diluted with water containing 50 ppm of Ca^{2+} to adjust the concentration of the oil proof agent to 1 % or with water containing 75 ppm of Ca^{2+} to adjust the concentration of the oil proof agent to 0.2 %. Then, each diluted emulsion was stirred at 3,000 ppm for 3 minutes. The condition of the emulsion was observed and evaluated according to the same criteria as used in Experiment 3. The results are shown in Table 5.

55

Experiment 7

A sizing effect of each of the emulsions of oil proof agents prepared in Experiment 6 was evaluated.

To a 60 g/l pulp suspension, as a bonding agent, Sumilets resin FR-2P (0.3 % per weight of pulp) and the oil proof composition (0.25, 0.30 or 0.35 % of solid materials per weight of pulp) was added to paper by the internal addition method. The average weight of paper was 60 g/m².

The sizing degree was measured in the same manner as in Experiment 4. The results are shown in Table 5.

Experiment 8

Oil resistance of the paper prepared in Experiment 7 was evaluated in the same manner as in Experiment 5.

The results are shown in Table 5.

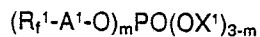
Table 5

Concentration of phosphate salt (%)	Dilution stability (CaCO ₃)		Sizing degree			Oil resistance		
	1	0.2	0.25	0.30	0.35	0.25	0.30	0.35
	Ca ²⁺ 50 ppm	Ca ²⁺ 75 ppm						
Example 10	O	Δ	3	6	8	8	12	12
Comparative Example 3	Δ	X	2	2	5	8	10	10

40 **Claims**

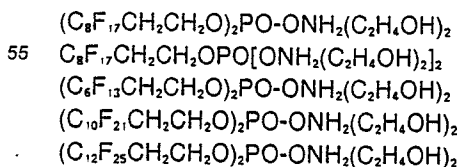
1. An oil proof composition for paper which comprises at least one salt selected from the group consisting of fluoroalkyl phosphate salts, N-alkyl fluoroalkanesulfonamidoalkyl phosphate salts and fluoroalkenyloxyaralkyl phosphonate salts and at least one anionic surfactant.

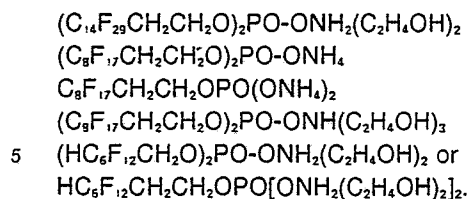
2. The oil proof composition according to claim 1, wherein the salt is a salt of fluoroalkyl phosphate of the formula:



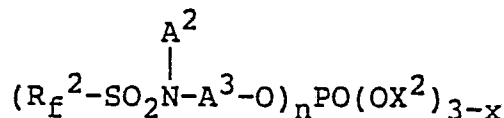
wherein R_f¹ is each a C₅-C₂₁ perfluoroalkyl or ω-hydroperfluoroalkyl group, A¹ is each a C₁-C₁₀ alkylene group, X¹ is an alkali metal or an ammonium group which may be substituted by a C₁-C₁₀ alkyl or hydroxyalkyl group, and m is 1 or 2.

3. The oil proof composition according to claim 2, wherein the salt of fluoroalkylphosphate is a salt of the formula:



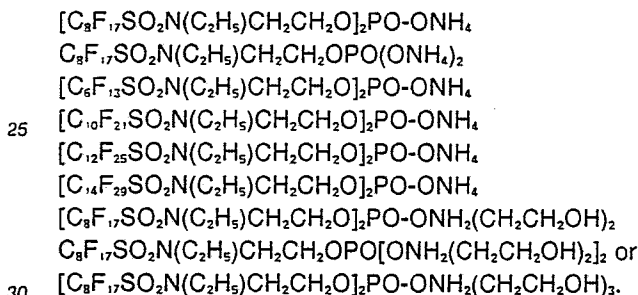


4. The oil proof composition according to claim 1, wherein the salt is a salt of N-alkyl fluoroalkanesulfonamidoalkyl phosphate of the formula:

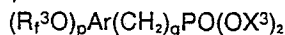


15 wherein R_F^2 is each a C_5 - C_{21} perfluoroalkyl group, A^2 is each a C_1 - C_{10} alkyl group, A^3 is each a C_1 - C_{10} alkylene group, X^2 is an alkali metal or an ammonium group which may be substituted by a C_1 - C_{10} alkyl or hydroxyalkyl group, and n is 1 or 2.

20 5. The oil proof composition according to claim 4, wherein the salt of N-alkyl fluoroalkanesulfonamidoalkyl phosphate is a salt of the formula:

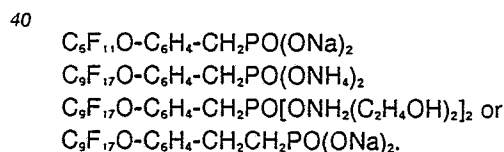


6. The oil proof composition according to claim 1, wherein the salt is a salt of fluoroalkenyloxyaralkyl phosphonate of the formula:



35 wherein R_F^3 is each a C_6 - C_{12} perfluoroalkenyl group, p is 1, 2 or 3 and Ar is an aromatic group which may have a substituent (e.g. phenyl, naphthyl, or alkyl-, acyl-, alkoxy- or halogen-substituted phenyl or naphthyl), q is 1 or 2 and X^3 is an alkali metal or an ammonium group which may be substituted by a C_1 - C_{10} alkyl or hydroxyalkyl group.

7. The oil proof composition according to claim 1, wherein the salt of fluoroalkenyloxyaralkyl phosphate is a salt of the formula:



45

50

55



EP 88 10 1967

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)
X	US-A-3 953 283 (J.H. WING et al.) * Claim 1 * ---	1,4,5	D 21 H 3/02
A	ABSTRACTS BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY, vol. 52, no. 11, May 1982, page 1347, abstract no. 12816, Appleton, Wisconsin, US; & JP-A-138 197/81 (DAIKIN TRADE & INDUSTRY CO.) 28-10-1981 * Whole abstract * ---	1-3	
A	GB-A-2 117 021 (SANDOZ PRODUCTS) * Abstract; page 1, lines 90-99 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			D 06 M D 21 H
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19-05-1988	Examiner 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	