

HYDROPHILICALLY AND LIPOPHILICALLY MODIFIED PERFLUOROPOLYETHERS AS INGREDIENTS OF NON-CONVENTIONAL COMPOSITIONS

Giovanni Pantini, Rossella Ingoglia, Solvay Solexis SpA - Personal Care Products

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INTRODUCTION

In recent years, the chemical modification of polymers has been a driving force in many industrial sectors. There was evidence that this might also be the case of perfluoropolyethers (PFPEs) in the personal care industry. To investigate this potential, a systematic study has been conducted at Solvay Solexis SpA (formerly Ausimont SpA), through the analysis of the organic chemistry suitable to modify PFPE structures, and through the examination of the properties of PFPE derivatives thus produced from the viewpoint of a cosmetic formulator.

Solvay Solexis chemistry involves the UV-light activated oxidative polymerization of perfluoro-olefins to yield liquid polymers, which are fractionated by molecular distillation. Two main classes of PFPEs are manufactured by Solvay Solexis:

- hexafluoropropene is used to produce Y-PFPEs, with a random structure and a much higher content of hexafluoropropene oxide units, and minor amounts of difluoromethylene oxide units;
- tetrafluoroethylene is used to produce Z-PFPEs, with a random structure and similar proportions of tetrafluoroethylene oxide units and difluoromethylene oxide units.

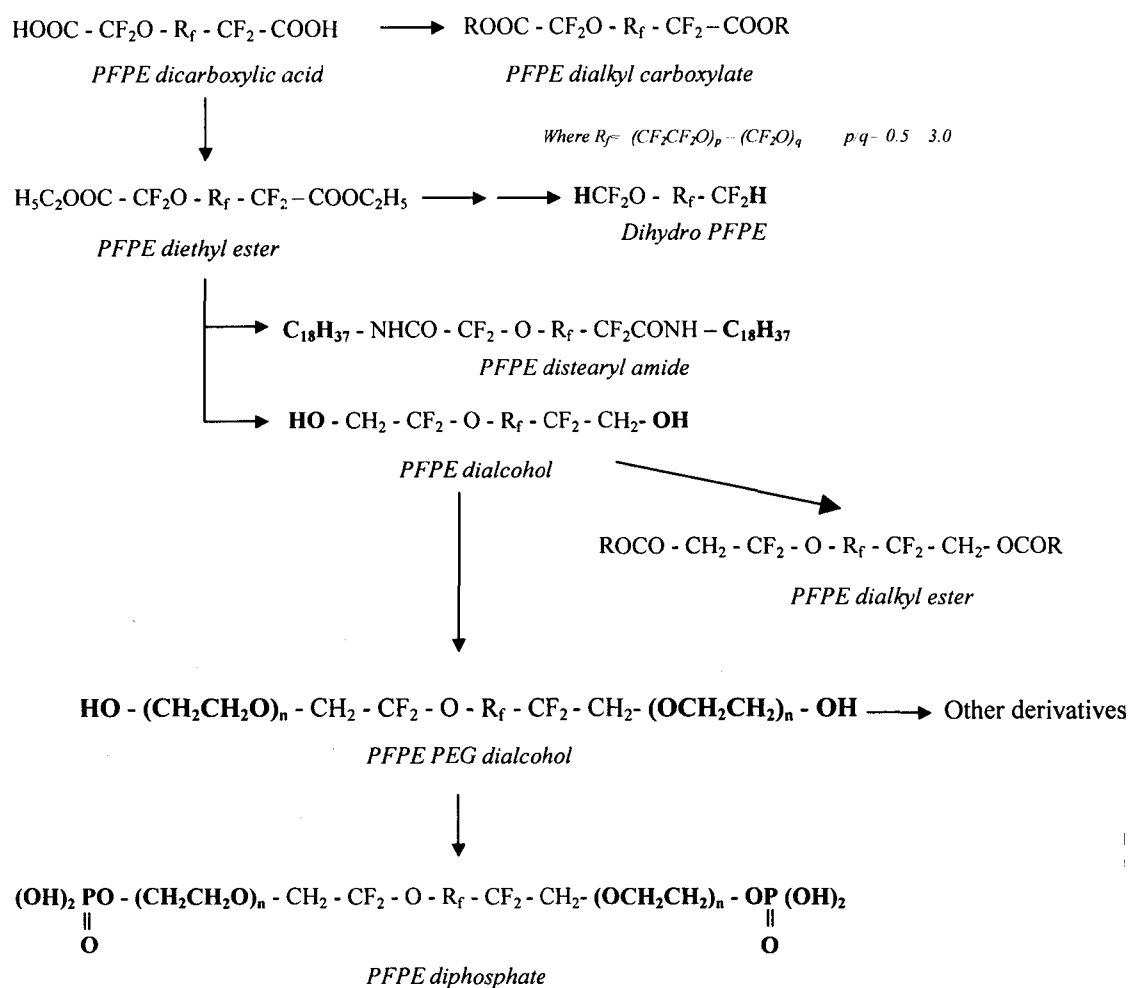
In the case of “neutral” (unmodified) materials for cosmetics, the Y-PFPE structure was chosen because of its higher fluorine content (68÷69%). And indeed Y-PFPEs, introduced in the personal care industry as “Perfluoropolymethylisopropyl Ether” and later renamed “Polyperfluoromethylisopropyl Ether” by the CTFA International Nomenclature Committee, proved to be suitable as cosmetic ingredients (1-5). On the other hand, the higher content of carbon-oxygen-carbon ether bonds and the absence of trifluoromethyl groups in Z-PFPEs give more flexible molecules, and consequently lower viscosity and melting points. For these reasons, the Z-structure was preferred to produce chemically modified PFPEs, in which only the terminal α - ω positions are modified. Most PFPE derivatives, prepared on a laboratory scale from Z-PFPE dicarboxylic acid ethyl esters and with a perfluorinated chain length from 500 to 2200, were indeed liquid or had low melting points, confirming that the chain flexibility is a critical factor concerning the physical form.

On the basis of the feasible chemistry (Figure 1) and of the manufacturing capability, the following classes of Z-PFPE derivatives (from now on simply PFPEs) appeared the most immediate candidates for an investigation as cosmetic materials:

- PFPE dicarboxylic acids,
- PFPE dialkylcarboxylates,
- Dihydro PFPEs,
- PFPE dialkylamides,
- PFPE dialcohols,
- PFPE dialkyl esters,
- PFPE PEG dialcohols,

- PFPE PEG diphosphates,
while other chemically modified PFPEs are in our programs of investigation.

Fig. 1 Scheme of synthesis of chemically modified perfluoropolyethers (PFPE) from a perfluoropolyether (PFPE) dicarboxylic acid as a building block.



Three classes of materials are unsuitable for cosmetic use: PFPE dicarboxylic acids because of their irritancy, PFPE dialkylcarboxylates and PFPE dialkyl esters (as well as other esters of PFPE dialcohols) because of the poor water stability (hydrolysis). Thus, five structures were selected for further study. The specific INCI name attributed to them are:

- Dihydro PFPEs: Polyperfluoroethoxymethoxy Difluoromethyl Ether,
- PFPE dialkylamides: Polyperfluoroethoxymethoxy Difluoromethyl Distearamide,
- PFPE dialcohols: Polyperfluoroethoxymethoxy Difluorohydroxyethyl Ether,
- PFPE PEG dialcohols: Polyperfluoroethoxymethoxy Difluoroethyl PEG Ether,
- PFPE PEG diphosphates: Polyperfluoroethoxymethoxy Difluoroethyl PEG Phosphate.

The preparation of ethoxylated PFPE derivatives (PEG dialcohols and PEG diphosphates), with a degree of ethoxylation higher than two proved unfeasible. Consequently, PFPE PEG-2 dialcohols and PFPE PEG-2 diphosphates were investigated.

MATERIALS AND METHODS

Materials

For each class of chemically modified Z-PFPEs (simply PFPEs), two grades were selected, combining the same chemical functionality with two different PFPE length chains. Only for the PFPE dialkylamides, the same PFPE chain is combined with two non-fluorinated moieties differing for the length of the alkyl chain – lauryl (C₁₂) or stearyl (C₁₈).

Table 1 Unmodified PFPEs vs chemically modified PFPEs: various combinations of the molecular weight and the chemical functionality, with a decreasing fluorine content.

Material	PFPE chain	Fluorine (%)	Chemical functionality (end chain)	Appearance (physical status)
<i>Unmodified PFPEs</i>				
Range of Y-PFPEs	650÷6250	69÷68	Trifluoromethyl	From volatile to viscous liquids (water-like)
Range of Z-PFPEs	500÷10000	66÷64	Trifluoromethyl	From volatile to viscous liquids (water-like)
<i>Dihydro PFPEs</i>				
Dihydro PFPE-130	500	64	Hydrogen	Low viscosity, volatile liquid (BP: 130°C)
Dihydro PFPE-180	650	64	Hydrogen	Low viscosity, volatile liquid (BP: 180°C)
<i>PFPE dialcohols</i>				
PFPE-1000 alcohol	1400	61	Hydroxy	Low viscosity, water-like liquid
PFPE-2000 alcohol	2200	62	Hydroxy	Low viscosity, water-like liquid
<i>PFPE PEG-2 dialcohols</i>				
PFPE-1000 PEG-2 alcohol	1400	56	Hydroxy	Low viscosity, water-like liquid
PFPE-2000 PEG-2 alcohol	2200	58	Hydroxy	Low viscosity, water-like liquid
<i>PFPE PEG-2diphosphates (*)</i>				
PFPE-1000 phosphate	1400	51	Phosphoric acid group	Light yellow transparent viscous liquid
PFPE-2000 phosphate	2200	53	Phosphoric acid group	Light yellow transparent viscous liquid
<i>PFPE dialkylamides</i>				
PFPE amide-12	1400	49	Lauryl group	Viscous light yellow liquid
PFPE amide-18	1400	45	Stearyl group	Light yellow waxy solid

Methods

Various methods were adopted for investigating the most relevant properties of compositions containing chemically modified PFPEs,

- *The filter paper test to evaluate the water (or oil) repellency*: absorption time of a droplet of water (or of mineral oil) applied to a filter paper treated with the composition (an in-house, simple but effective method particularly suitable for screening work);
- *The test on the resistance (of sunscreens) to wash-off*: UV spectroscopy measurements (by a UV/Vis Jasco V 530 spectrophotometer) of the amounts of the UV chemical filter removed from the arms of four volunteers, comparing the amount (of UV filter) from the immersed arm with the amount from the non-immersed arm (a method derived from a FDA protocol);
- *Skin irritation test (on self-tanners or other acidic compositions)*: occlusive patch test on 20 volunteers, with the composition applied to the skin for 8 hours, and the evaluation of the skin reaction 15 minutes and 2 hours after the removal of the patches (a protocol of the Cosmetic Technology and Science School, Ferrara University, Ferrara, Italy);
- *Microbial challenge test*: each composition is challenged separately with the following micro-organisms: Escherichia coli, Staphylococcus aureus, Pseudomonas aeruginosa, Candida albicans; with bacteria and Candida albicans at 10⁶ to 10⁷ and at 10⁵ to 10⁶ CFU/ml of the composition, respectively (a protocol of the Institute of Microbiology, Ferrara University, Ferrara, Italy, derived from a CTFA protocol).

(*) The two grades of PFPE PEG-2 diphosphates are named simply PFPE-1000 phosphate and PFPE-2000 phosphate since the corresponding non-ethoxylated grades, that theoretically could be prepared from PFPE dialcohols, are not stable and therefore there is no possibility of confusion.

EXPERIMENTAL PART

Solubility in an oily or in an aqueous phase, and dispersability in glycerin and mutual compatibility, have been considered because of the importance of these properties for the formulating potential of chemically modified PFPEs (Table 2).

Table 2 Solubility properties and dispersability of chemically modified PFPEs

Material	Oil/ water solubility, or solubilization power or dispersability (in glycerin)
<i>Dihydro PFPEs</i>	
Dihydro PFPE-130	Oil/water insoluble, solvent of PFPE amide-12, and of PFPE amide-18 (partially);
Dihydro PFPE-180	Oil/water insoluble, solvent of PFPE amide-12, and of PFPE amide-18 (partially);
<i>PFPE dialcohols</i>	
PFPE-1000 alcohol	Oil/water insoluble, easy dispersability in glycerin (and other polyhydric alcohols);
PFPE-2000 alcohol	Oil/water insoluble, easy dispersability in glycerin (and other polyhydric alcohols);
<i>PFPE PEG-2 dialcohols</i>	
PFPE-1000 PEG-2 alcohol	Oil/water insoluble, easy dispersability in glycerin (and other polyhydric alcohols);
PFPE-2000 PEG-2 alcohol	Oil/water insoluble, easy dispersability in glycerin (and other polyhydric alcohols);
<i>PFPE PEG-2 diphosphates</i>	
PFPE-1000 phosphate	Soluble in polar solvents (alcohols, glycols) producing solutions that can be diluted with water, soluble directly in water by partial neutralization with sodium hydroxide, insoluble in oils;
PFPE-2000 phosphate	Soluble in polar solvents (alcohols, glycols) producing solutions that can be diluted with water, soluble directly in water by partial neutralization with sodium hydroxide, insoluble in oils;
<i>PFPE dialkylamides</i>	
PFPE amide-12	Soluble in some polar oils and in dihydro PFPEs, insoluble in apolar oils and water;
PFPE amide-18	Soluble (> 50°C) in most polar oils or combinations of polar/apolar oils producing lipogels (20°C), soluble in aprotic solvents at room temperature, insoluble in apolar oils and water.

On the basis of solubility, solubilization and dispersability properties, various bicomponent compositions were prepared, as reported in table 3:

Table 3 Bicomponent compositions (solutions, gels, dispersions), containing a chemically modified PFPE, to be used for preparing more complex compositions.

Material\Other component	Polar oils ¹	Glycerin ²	Solvents	Water
<i>Dihydro PFPEs</i>				
Dihydro PFPE-130	-	-	Ethanol solutions ³	-
Dihydro PFPE-180	-	-	Ethanol solutions ³	-
<i>PFPE dialcohols</i>				
PFPE-1000 alcohol	-	Stable dispersions	- ⁴	-
PFPE-2000 alcohol	-	Stable dispersions	- ⁴	-
<i>PFPE PEG-2 dialcohols</i>				
PFPE-1000 PEG-2 alcohol	-	Stable dispersions	- ⁴	-
PFPE-2000 PEG-2 alcohol	-	Stable dispersions	- ⁴	-
<i>PFPE PEG-2 phosphates</i>				
PFPE-1000 phosphate	-	Stable dispersions	Acidic solutions ⁵	Solutions ⁶
PFPE-2000 phosphate	-	Stable dispersions	Acidic solutions ⁵	Solutions ⁶
<i>PFPE dialkylamides</i>				
PFPE amide-12	-	-	Isopropanol solutions ³	-
PFPE amide-18	Lipogels	-	Isopropanol solutions ³	-

¹ A polar oil or an oily phase with polar oils as the major part.

² Glycerin can be replaced by another polyhydric alcohol, for preparing stable dispersions (emulsions) without using emulsifiers.

³ The addition of water causes the separation of the PFPE.

⁴ Partially soluble in alcohols - the addition of water causes the complete separation of the PFPE.

⁵ Concentrated solutions (up to 40%) in polar solvents (alcohols, glycols, etc.) that can be diluted with water without separation.

⁶ Transparent aqueous solutions prepared by neutralization with sodium hydroxide (or an amine) of PFPE dispersions in water.

From these simple compositions, more complex compositions were prepared (Table 4).

Table 4 The use of chemical modified PFPEs for an easier or non-conventional formulating and for improved performances (vs unmodified PFPEs).

Chemically modified PFPE	Other main ingredients	Composition
Dihydro PFPE-130 or Dihydro PFPE-180	Common emulsifiers, polar and apolar oils	Triphase emulsions (F+O/W) ¹
PFPE-1000 alcohol or PFPE-2000 alcohol	Pigments and powders	Oil-free compact powders
PFPE-1000 alcohol or PFPE-2000 alcohol or a PFPE PEG-2 alcohol	Glycerin	Newtonian F/G emulsions, without emulsifiers (F = PFPE-1000 alcohol, G = glycerin)
PFPE-1000 alcohol or PFPE-2000 alcohol or a PFPE PEG-2 alcohol	Glycerin and oils (O ₁ and O ₂)	(O ₁ +F)/G triphase emulsions, (O ₁ +F)G/O ₂ multiple emulsions where: O ₁ = or ≠ O ₂
PFPE-1000 phosphate (PFPE-2000 phosphate)	Alcohol, pigments and powders	Coated pigments/powders for make-up products with higher persistence and uniformity
PFPE-1000 phosphate (PFPE-2000 phosphate)	Alcohols or glycols (and xanthan gum)	Acidic (pH = 3) non-irritant, self-preserved hydrosolutions (and transparent hydrogels)
PFPE-1000 phosphate (PFPE-2000 phosphate)	Glycols or alcohols, and polar oils	Acidic (pH = 3) superfluid, self-preserved emulsions with viscosity lower than 5 mPa.s.
PFPE-1000 phosphate (PFPE-2000 phosphate)	Sodium hydroxide (or amine)	Transparent, self-preserved carbomer hydrogels
PFPE-1000 phosphate (PFPE-2000 phosphate)	Sodium hydroxide (or amine) and polar oils	Superfluid O/W emulsions stabilized by micronization with high pressure homogenizers
PFPE-1000 phosphate (PFPE-2000 phosphate)	Sodium hydroxide and polar oils, dihydro PFPE-130 (or PFPE-180)	Superfluid O/W emulsions stabilized by addition of dihydro PFPE-130 or dihydro PFPE-180
PFPE-1000 phosphate (PFPE-2000 phosphate)	Sodium hydroxide, polar oils, UV filters	Superfluid sunscreen emulsions resistant to wash-off
PFPE amide-12	Dihydro PFPE-130 (or PFPE-180) and polar oils	PFPE amide-12 is soluble in dihydro PFPE-130, but no emulsification occurs by addition of polar oils.
PFPE amide-18	Aprotic solvents (acetone, ethyl/butylacetate, methylethylketone)	Anhydrous solutions (eg nail enamel removers) (a dihydro PFPE can be added)
PFPE amide-18	Major part of polar oils and minor part of apolar oils	Lipogels (and sticks) with high water repellency and some oil repellency
PFPE amide-18	Alkylated acrylic acid polymers, polar and apolar oils (UV filters)	Fluid/viscous gel-emulsions with high water/oil repellency (skin protectants against irritants, water resistant sunscreens)
PFPE amide-18	Major part of polar oils and minor part of apolar oils	Surfactant-free W/O emulsions with high water/oil repellency (water resistant sunscreens with UV chemical filters)
PFPE amide-18	Dihydro PFPE-130 (or PFPE-180) and polar oils	F/O emulsions ² (intermediates for F/O/W multiple emulsions) with the amide (solubilized in the oils) as a F/O emulsifier
PFPE amide-18 PFPE-1000 phosphate	Dihydro PFPE-130 and polar oils, then sodium hydroxide	From F/O emulsions ² to superfluid multiple F/O/W emulsions ² (highly water/oil repellent) with PFPE-1000 phosphate solubilized in water as a O/W emulsifier
PFPE-1000 phosphate PFPE amide-18	Sodium hydroxide, polar oils, and dihydro PFPE-130	Superfluid O/W emulsions with PFPE-1000 phosphate are stabilized by a dihydro PFPE, then PFPE amide-18 is added

(or dihydro PFPE-180)

to have highly water/oil repellent O+F/W emulsions²

¹ Triphase emulsions are usually obtained with any chemically modified PFPE if specific formulating procedures are not adopted.

² In these emulsions, F = dihydro PFPE.

RESULTS AND DISCUSSIONS

Besides other properties, hydrophobicity (water repellency) combined with lipophobicity (oil repellency) and insolubility make perfluoropolyethers (simply PFPEs) a unique class of cosmetic materials. In spite of their insolubility and high density (almost twice of water), PFPEs can be formulated with common emulsifiers and techniques, producing storage stable emulsions (named "triphase" since the PFPE is an additional dispersed phase), that basically are not procedure-dependent (1-3). PFPEs can also be formulated as ingredients of non-oily compositions, such as translucent shampoos and hydrogels, by predispersing them in glycerin (6). From these concentrated premixes (up to 30%), prepared simply by mixing a PFPE and glycerin at room temperature in the presence of a small quantity of an emulsifier (preferably ionic), anhydrous triphase (O₁+F)/G and multiple (O₁+F)G/O₂ emulsions can be produced by combination with oils (7). In the triphase and glycerin-based emulsions, the PFPE is an ingredient of compositions which have their own structural agents, common emulsifiers (usually combined with hydrophilic thickeners) and glycerin. These agents might alter the functionality of compositions containing the PFPE, particularly the water/oil repellency properties of skin protectants (against irritants) and the resistance of sunscreens to wash-off.

This was the rationale of the first research work (8) and the following ones aimed at developing new cosmetic materials, through the chemical modification of PFPEs. These new materials should have had at least more compatibility, wetting power and substantivity, and ideally combine solubilization in an aqueous or in an oily phase while behaving as structurants or stabilizers and retaining or enhancing the performances of unmodified PFPEs. To achieve these objectives, Z-PFPEs (prepared from tetrafluoroethylene) were preferred over Y-PFPEs (prepared from hexafluoro-propene), because of the higher content of ether bonds (a positive factor with in mind the objective of liquid materials and better compatibility), and the greater impact of the α - ω disubstitution (instead of the former monosubstitution achievable with the Y-PFPEs).

It is remarkable that a very small chemical modification, the replacement of a fluorine atom with a hydrogen atom at the terminal α - ω positions, enables to create a certain degree of polarity. This polarity is sufficient to impart solubility in alcohols (while the corresponding unmodified PFPEs are completely insoluble) and remarkably higher compatibility with most common cosmetic ingredients (particularly with the polar ones), provided that the molecular weight of the PFPE chain is low (in the 500-650 range). However, solubility in an aqueous phase or in an oily phase is not achieved. Consequently, dihydro PFPEs should be formulated as insoluble materials, for preparing triphase emulsions. In these emulsions, dihydro PFPE-130 and dihydro PFPE-180 work as transient emollients because of the volatility, in spite of relatively high boiling points (130°C and 180°C, respectively). Furthermore, because of their higher compatibility, dihydro PFPEs can be used to formulate innovative emulsions, in combination with other chemically modified PFPEs, as shown below.

The introduction of hydroxy groups (by reducing PFPE dicarboxylic acid ethyl esters to PFPE dialcohols) is expected to give more polarity (hence hydrophilic character) to the molecule. Theoretically, further hydrophilicity could be achieved by ethoxylation of PFPE alcohols, but PFPE ethoxylated derivatives with a degree of ethoxylation higher than two are not stable. Nevertheless, it is possible to modify the behavior of a longer PFPE chain, ranging from 1400 to 2200 molecular weight. PFPE dialcohols and the corresponding PEG-2 derivatives have indeed improved compatibility with common cosmetic materials, higher wetting power and substantivity towards various substrates, and even partial solubility in

polar solvents, e.g. alcohols (but complete separation and stratification occur by addition of water).

These properties reach a maximum in PFPE-1000 alcohol in comparison either with PFPE-2000 alcohol (for the higher content of the hydroxy groups of the former), and with the two PEG-2 alcohols (for the lower acidity of ethoxylated alcohols). The potential of PFPE-1000 alcohol is demonstrated by the preparation of stable dispersions in glycerin (or other polyhydric alcohols) without the use of emulsifiers (needed when unmodified PFPEs are used). From these Newtonian F/G emulsions, it is possible to prepare triphase $(O_1+F)G$ and multiple $(O_1+F)G/O_2$ emulsions by combination with oils – addition of O_1 to the F/G emulsion and addition of the $(O_1+F)G$ emulsion to O_2 . While these multiphase emulsions may be regarded with a speculative interest, the premixing in glycerin is a practical and simple method to introduce PFPE-1000 alcohol in shampoos and hydrogels, where it works as a hair shining agent or a skin conditioner. The wetting power of PFPE-1000 alcohol can be exploited in other formulations, for example in compact powders, where it can be used as such (or combined with oils) as a binding agent.

The modification with phosphate groups is expected to impart the stronger polarity that is necessary to have solubilization in polar solvents and even to pull a perfluoropolyether moiety into aqueous solutions. And indeed PFPE diphosphates can be solubilized in alcohols, glycols, and other polar solvents, producing concentrated solutions (up to 40%), irrespectively from the molecular weight of the PFPE. The use of alcohol solutions of a PFPE diphosphate for coating pigments and mineral powders for make-up products was the first application when these PFPEs were synthesized. The hydrophobic and lipophobic pigments and powders produced in this way show improved persistence and make-up uniformity on the skin.

Perhaps more important for the formulator is the possibility to dilute the concentrated solutions (in polar solvents) of PFPE diphosphates, by careful addition of a much larger proportion of water (9,10). The unneutralized solutions of PFPE diphosphates have a pH ranging from 2 to 3. Xanthan gum gels and emulsions can be prepared from these acidic solutions without neutralization. The compositions (aqueous solutions, gels and emulsions) proved (patch tests on volunteers) to be non-irritant, contrary to what happens with low pH formulations of very mild organic acid, e.g. lactic acid. Non irritant acid compositions are ideal for various functional ingredients that are more stable or more effective at a low pH, such as dihydroxyacetone in self-tanners (11), or vitamin A, polyphenols, and alpha-hydroxy acids in facial products.

As expected, the neutralization of the phosphate group further increases the polarity and consequently the solubility. Indeed, by partial neutralization with sodium hydroxide (or another base) of the water dispersions it is possible to solubilize PFPE diphosphates directly in water, without the use of any solvent. Transparent solutions with a pH ranging from 5 to 7 are obtained (9,10). The availability of water solutions with the suitable concentration (0.1÷2.0%) of a PFPE diphosphate and a physiological pH is a route for preparing carbomer gels. These gels show high oil repellency, hence skin protection against oil soluble irritants, and prevent the transfer of make-up products, particularly lipsticks, when they are applied over. From the water solutions of PFPE diphosphates, O/W emulsions also may be prepared. In these emulsions, PFPE diphosphates work as primary emulsifiers producing superfluid emulsions (ie emulsions with viscosity lower than 5 mPa.s.), even with a high oil content.

The multifunctionality of PFPE diphosphates was further demonstrated by their activity as antimicrobial agents against bacteria and yeasts over a wide range of pH, with and without alcohols or glycols. This shows high potential for non-conventional, preservative-free systems. It is well-known that to have preservation solvents (such as alcohols and glycols) must be used at relatively high levels, e.g. pentylene glycol is effective only at concentrations higher than 5%, and even then it has no actions against gram-positive bacteria. It is remarkable that the combination of pentylene glycol and PFPE-1000 phosphate proved to be effective against a broad spectrum of micro-organisms, including gram-positive bacteria, when the two ingredients were used at 1% (9,10).

While a molecular weight in the 1400 ÷ 2200 does not modify remarkably properties such as solubility and viscosity, the emulsifying and antimicrobial activity appear to be more dependent on the PFPE chain length, with PFPE-2000 phosphate less effective in both cases. Therefore, PFPE-1000 phosphate was investigated more in detail, particularly as a primary emulsifier for producing superfluid O/W emulsions. Designed without using surfactants, these emulsions are suitable as skin protectants (being water/oil repellent) and as sunscreens (being resistant to the wash-off), in the form of sprays or impregnated wipes. Because the extremely low viscosity, creaming or sedimentation during storage must be prevented - this can be done by increasing the viscosity of the continuous phase, or by decreasing the difference in density between the continuous and the dispersed phase, or by micronization with a high pressure homogenizer (12). Unexpectedly, the addition of a dihydro PFPE proved to be a simple method to stabilize superfluid emulsions. The reasons why this happens and the potential consequences need further investigation, since the experimental observations are in contradiction with what may be expected, e.g. from the Stoke's law, since the density of dihydro PFPEs is about 1.7, and much higher than that one of the continuous phase.

The introduction of an alkyl group at the end of the chain might give lipophilicity to the PFPEs, and it should be expected that the longer the hydrocarbon chain, the higher the lipophilicity. A simple way to have alkyl-substitution is to react a PFPE dicarboxylic acid with a primary alkyl amine, producing PFPE dialkyl amides. These materials contain a perfluorinated moiety (typically hydrophobic and lipophobic) and a hydrocarbon moiety (typically hydrophobic) and they should show strong hydrophobicity and some lipophobicity. To evaluate the most suitable hydrocarbon chain, the properties of PFPE amide-12 and PFPE amide-18, prepared from lauryl amine and stearyl amine of vegetable origin and from a PFPE of about 1400 molecular weight, were compared.

PFPE amide-18, a waxy material with a low melting point (53°C), proved to be lipophilic and soluble in most hot polar oils (or oil combinations, where polar oils are the main component and apolar oils are a minor part). Cooling down these solutions to room temperature, stable lipogels are obtained. Therefore, the oil solubilization is a general route for formulating PFPE amide-18 as an ingredient of conventional compositions, including lipsticks, O/W and W/O emulsions with common emulsifiers. Furthermore, alkylated acrylic acid polymers or other polymeric emulsifiers may be used for preparing gel-emulsions. In these compositions, PFPE amide-18 works also as a structurant and may replace common hydrophilic thickeners because of its viscosity-building properties. Thus, the water/oil repellency of skin protectants (filter paper test) and the resistance to wash-off of sunscreens (water resistant test) are retained (13) – in particular, in the case of alkylated polymeric

emulsifiers, gel-emulsions of variable viscosity are produced, depending of the degree of alkylation of the emulsifier.

The activity of PFPE amide-18 as a primary emulsifier for the preparation of non-conventional emulsions is not completely unexpected if one considers its chemical structure. At high temperature, PFPE amide-18 is effective, and without other structurants, for preparing surfactants-free W/O emulsions (where the oily phase is made essentially of polar oils). PFPE amide-18 may be used also as a primary emulsifier for dispersing a dihydro PFPE in an oily phase, producing F/O emulsions. In another area of formulation, the solubility at room temperature in aprotic volatile solvents (such as acetone, methylethyl ketone, ethyl acetate, butyl acetate, etc.) suggests the use of PFPE amide-18 in nail care, as a superfatting agent of enamel removers. The solubility of PFPE amide-18 in surfactants, particularly non-ionic and amphoteric surfactants also, deserves a deeper investigation.

The liquid form suggested to investigate PFPE amide-12 for potential advantages in comparison with PFPE amide-18 (14). In spite of its lower lipophilicity, PFPE amide-12 is soluble in hot oils (but at room temperature, separation occurs). Because of its higher fluorine content (49% vs 45%), PFPE amide-12 is also soluble in dihydro PFPEs (and as expected more than PFPE amide-18). However, while PFPE amide-18 may be used as a primary emulsifier for dispersing a dihydro PFPE in an oily phase (F/O emulsions), PFPE amide-12 proved to be ineffective either as an emulsifier for preparing O/F emulsions (dispersions of oils in a dihydro PFPE), or as a viscosity-building agent (for preparing gels of dihydro PFPEs). Therefore, PFPE amide-12 does not show advantages attributable to its higher fluorophilic character.

The combined use of chemically modified PFPEs is at the same time a challenge and an opportunity to formulators. We have already mentioned the use of PFPE amide-18 for preparing F/O emulsions. These emulsions can be further dispersed in a homogeneous liquid phase (water) containing PFPE-1000 phosphate, producing superfluid multiple F/O/W emulsions. There are various other ways to combine PFPE-1000 phosphate with PFPE amide-18 (without considering that dihydro PFPEs can be added with different procedures). The phosphate may be used as a primary emulsifier, and the amide may be added as water/oil repellent agent, either by solubilization in the oily phase before emulsification, or during emulsification such that a separate phase is formed. Alternatively, the primary emulsifier may be a conventional emulsifier or an alkylated acrylic acid polymer, and PFPE-1000 phosphate and PFPE amide-18 are added in different proportions to increase respectively oil repellency and water repellency. A drawback of these combinations is that the antimicrobial properties of PFPE-1000 phosphate are negatively affected by PFPE amide-18, probably because a chemical reaction occurs.

CONCLUSIONS

The chemical modification of PFPEs is a powerful tool for developing new cosmetic materials, in the context of non-conventional compositions and of unique combinations of performances. Our investigation, that is still underway, has shown that:

- it is possible to prepare many and very different compositions, from hydroalcoholic solutions to aqueous and anhydrous solutions, from hydrogels to lipogels, from superfluid O/W emulsions to W/O emulsions and various types of multiple emulsions, with a pH ranging from 3 to 7. The main field of application is skin care, but there is potential also for other personal care formulations, e.g. make-up and toiletry products, hair care.
- an increase of the formulating potential is due to the possibility to have solubilization only in specific conditions and when precise procedures are adopted, such that very different compositions can be prepared by simply changing the procedure.
- it should be noted that in spite of their lower fluorine content (and it is the fluorine atoms the reason of water/oil repellency of perfluoropolymers), chemically modified PFPEs are more effective than unmodified PFPEs in developing water/oil repellency properties. This is probably due to two reasons: the special design of the compositions (without ingredients that affects the behavior of PFPEs) and the higher substantivity.
- PFPE-1000 phosphate shows extremely high oil repellency, while PFPE amide-18 shows either high water repellency and a very good combination of water and oil repellency. It is therefore possible to modulate the water/oil repellency properties, and to formulate multipurpose protective emulsions or more tailored emulsions for the protection of the skin against water or oil soluble irritants.
- the resistance of sunscreens to wash-off seems more related to the design of the formulation (without common emulsifiers and thickeners in a way that re-emulsification does not occur) than to its water repellency. As a matter of illustration, we mention that superfluid sunscreen O/W emulsions (based on PFPE-1000 phosphate) have resistance to wash-off at least comparable with that one of W/O sunscreen emulsions (based on PFPE amide-18), in spite of the latter are remarkably more water repellent.
- chemically modified PFPEs behave as multifunctional ingredients, with additional performances (vs unmodified PFPEs) due to synergisms between the polymeric structure and the chemical group (eg PFPE-1000 phosphate is a non-irritant acid and an antimicrobial agent, PFPE SA-18 is a viscosity agent, and both are also primary emulsifiers in some conditions).
- when combining a PFPE chain with a chemical group or a hydrocarbon chain, the latter is more critical than the former. The differences in the physical form, formulation capability and performances between the two series of PFPE derivatives (with 1400 and 2200 PFPE molecular weight, 60% difference) are indeed minimal. On the contrary, PFPE stearyl amide has a different physical form and behaves differently from PFPE lauryl amide, in spite of the same PFPE chain length (1400), simply because the 50% difference in the hydrocarbon chain length.

There are many more chemical modifications to investigate, either to impart hydrophilic or lipophilic characters. This may lead to new compositions or to the discovery of new performance features, or to improve the stability or the sensorial properties of cosmetic formulations. Among the fields to be explored, we can mention a water soluble PFPE quaternary ammonium compound, a liquid PFPE alkyl ester, and an alkoxyated PFPE derivative.

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Corresponding author: *Dr Giovanni Pantini, Solvay Solexis SpA, Personal Care Products
Viale Lombardia 20, I-20021 Bollate (MI)*

Phone: +39-02-3835.2135, fax: +39-02-3835.2129, e-mail: giovanni.pantini@solvay.com