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54 **Lubricants for use in the plastic processing of metals.**

57 Aqueous compositions containing from 1% to 40% by weight of a perfluoropolyether compound having a molecular weight ranging from 400 to 5,000 and containing carboxylic end groups, which are salified with an organic or inorganic base, said compositions being useful as lubricating/refrigerating liquids in the plastic cold processing processes of metals, in particular rolling, dishing, drawing and the like.

**EP 0 360 503 A1**

## LUBRICANTS FOR USE IN THE PLASTIC PROCESSING OF METALS

The present invention relates to a liquid water-based composition useful as a lubricating and refrigerating liquid in the plastic processing of metals, which comprises, as a basic ingredient, a perfluoropolyether compound. The composition according to the invention is suitable in particular for rolling, dishing, drawing, pressing of metals in general, of ferrous and non-ferrous types such as steel, copper, aluminium and alloys thereof.

The use of liquids acting as lubricants in metal processing processes is well known. Such liquids, which generally consist of hydrocarbon oils with various additives for improving the performances thereof under severe operative conditions (high pressures, high temperatures), exhibit the drawback of being inflammable.

Recently, the use of aqueous emulsion with components having lubricating properties has been suggested. Such products are practically unaffected by the drawback of being inflammable under the operating conditions, and also satisfactorily fulfil the task of cooling the materials being processed. Lubricating compositions of this type are described for example in EP-A-0,048,216 (Alusuisse) CA-A-987,655 (Exxon), US-A-4,585,565 (Alcoa) and US-A-4,618,441 (Alcoa). Although many compositions in the form of aqueous emulsions have been suggested, it has been found that it is very difficult to prepare a composition which exhibits excellent performances as regards lubrication and cooling, a low friction coefficient (in order to achieve high reduction ratios) and which, furthermore, is endowed with good lubricating properties at high pressures and at the same time is free from various drawbacks such as instability of the emulsion which can lead to separation under the operating conditions.

The known compositions always require specific additives depending on the fields of use, in order to attain good values for the specific properties which are of major interest for the expected use.

A new metal processing composition according to the invention is an aqueous composition comprising from 1 to 40% by weight of a perfluoropolyether compound having an average molecular weight of at least 400 with end groups of the perfluoropolyether chain consisting of perfluoroalkyls and/or functional groups.

The composition of the invention, besides exerting an excellent lubricating action, which allows a large reduction of thickness in a single run or pass in the rolling process, also effect an efficacious cooling of the material being processed by virtue of the high water content of the composition. The water content is at least 60% by weight and is preferably at least 80% by weight.

Furthermore, the compositions do not leave harmful product residues on the processed material, in a few cases it being possible to avoid a subsequent washing or rinsing. The compositions according to the invention possess a high chemical stability and, if they are in the form of microemulsions, an unlimited physical stability. In addition, the residues remaining after evaporation of the water are non-inflammable.

An essential component of the lubricating-refrigerating compositions according to the invention is a perfluoropolyether (PFPE) having an average molecular weight of at least 400 and preferably not higher than 5,000, with end groups of the perfluoropolyether chain of neutral type (perfluoroalkyl groups) and/or of polar functional type. The perfluoropolyether compound may be present in the aqueous composition either in the form of solution when the average molecular weight does not exceed 1,000 and the end groups are particularly hydrophilic (carboxylic groups), or in the form of microemulsions when the molecular weight exceeds 1,000 or alternatively when the average molecular weight is low and the end groups are neutral (perfluoroalkyl groups). The term "microemulsion" designates a liquid, macroscopically single-phase composition, which is limpid (transparent) or slightly opalescent (translucent), optically isotropic, indefinitely stable in a defined temperature range comprising the temperature at which said composition is used.

The microemulsions of both neutral and functional perfluoropolyether are prepared according to the earlier patent application EP-A-0,250,766.

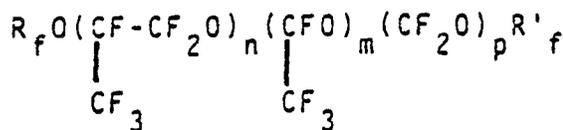
Perfluoropolyether compounds which are particularly suitable as basic components of the aqueous composition of the present invention are the ones having a carboxylic end group suitably saltified with organic or inorganic bases, in particular with ammonia or triethanolamine.

The amount of total perfluoropolyether compounds in the lubricating composition according to the invention ranges from 1% to 40% by weight, preferably from 2% to 20%.

The perfluoropolyethers suited to form the lubricating compositions which are the object of the present invention are in particular the ones which have an average molecular weight from 400 to 5,000 and preferably from 600 to 2,000, and belong in particular to one or more of the following classes:

1)

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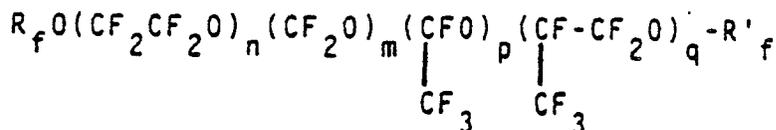


with a random distribution of the perfluoroxyalkylene units, wherein  $R_f$  and  $R'_f$ , like or different from each other, are  $-\text{CF}_3$ -,  $-\text{C}_2\text{F}_5$ -,  $-\text{C}_3\text{F}_7$ -, or  $-\text{COOH}$ -,  $-\text{CF}_2\text{COOH}$ -, and  $m$ ,  $n$ ,  $p$  have such values as to meet the aforesaid average molecular weight requirements;

2)  $R_f O (\text{CF}_2 \text{CF}_2 \text{O})_n (\text{CF}_2 \text{O})_m R'_f$ , with a random distribution of the perfluoroxyalkylene units, wherein  $R_f$  and  $R'_f$ , like or different from each other, are  $-\text{CF}_3$  or  $-\text{C}_2\text{F}_5$ -, or  $-\text{COOH}$ -,  $-\text{CF}_2\text{COOH}$  and  $m$  and  $n$  have such values as to meet the abovesaid requirements;

3)

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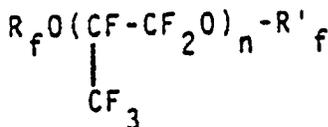
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with a random distribution of the perfluoroxyalkylene units, wherein  $R_f$  and  $R'_f$  like or different from each other, are  $-\text{CF}_3$ -,  $-\text{C}_2\text{F}_5$  or  $-\text{C}_3\text{F}_7$ -, or one of the above-indicated carboxylic radicals, and  $m$ ,  $n$ ,  $p$ ,  $q$  have such values as to meet the abovesaid requirements;

25

4)

30



wherein  $R_f$  or  $R'_f$ , like or different from each other, are  $-\text{C}_2\text{F}_5$  or  $-\text{C}_3\text{F}_7$  or one of the above-indicated carboxylic radicals, and  $n$  has such a value as to meet the abovesaid requirements;

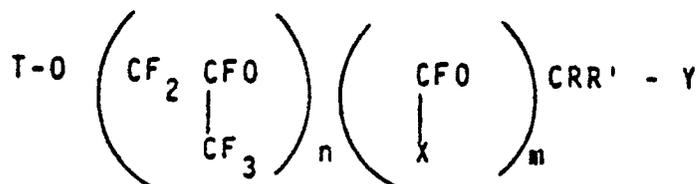
5)  $R_f O (\text{CF}_2 \text{CF}_2 \text{O})_n R'_f$  wherein  $R_f$  and  $R'_f$ , like or different from each other, are  $-\text{CF}_3$ -,  $-\text{C}_2\text{F}_5$ -, or one of the above-indicated carboxylic radicals, and  $n$  has such a value as to meet the abovesaid requirements;

6)  $R_f O (\text{CX}_2 \text{CF}_2 \text{CF}_2 \text{O})_n R'_f$  wherein  $R_f$  and  $R'_f$ , like or different from each other, are  $-\text{CF}_3$  or  $-\text{C}_2\text{F}_5$  or  $-\text{C}_3\text{F}_7$  or one of the above-indicated carboxylic radicals,  $X$  is  $F$  or  $H$ ,  $n$  having such a value as to meet the abovesaid requirements;

40

7)

45



wherein  $X$  is  $F$  or  $\text{CF}_3$ ,  $R$  is  $F$  or  $\text{Cl}$  or  $\text{Br}$  or  $\text{I}$ ,  $R'$ , like or different from  $R$ , is also  $F$  or  $\text{Cl}$  or  $\text{Br}$  or  $\text{I}$ ,  $Y$  is a  $-\text{COOH}$  group or a perfluoroalkyl group,

$T$  is a perfluoroalkyl group containing one or two atoms of  $\text{Cl}$  or  $\text{Br}$  or  $\text{I}$ ; in particular it may be  $\text{Alog CF}_2$ -,  $\text{Alog CF}_2 \text{CF}$ -

55

where  $\text{Alog}$  is  $\text{Cl}$  or  $\text{Br}$  or  $\text{I}$ ,

$n$  ranges from 1 to 15, the  $m/n$  ratio ranging from 0.01 to 0.5.

Perfluoropolyethers of class 1) are commercially available under the trademarks Fomblin<sup>®</sup> or Galden<sup>®</sup>

and those of class 2) are commercially available under the trademark Fomblin<sup>®</sup>Z, all being produced by Montedison.

Products of class 4), which are available on the market are the Krytox<sup>®</sup> (du Pont). Products of class 5) are described in US-A-4,523,039 or in J. Am. Chem. Soc. 1985, 107, 1197-1201.

5 Products of class 6) are described in EP-A-0,148,482 in the name of Daikin.

The products of class 3) are prepared according to US-A-3,665,041. The products of class 7) are described in Italian patent applications Nos. 20,406 A/88 and 20,407 A/88 in the name of the present applicant.

10 A second inessential but still very useful ingredient, in particular in order to increase the stability of the aqueous microemulsion when it contains non functional (neutral) PFPE, is a hydrogenated aliphatic alcohol, in particular isopropanol, or a fluorinated alcohol such as perfluoropolyether with end group -OH and a low molecular weight ( $\leq 450$ ).

The alcohol amount in the aqueous composition may be as much as 20% by weight, but usually it does not exceed 10%. Useful compositions are described in previously cited EP-A-0,250,766.

15 The lubricating composition according to the invention may furthermore contain small amounts of conventional additives such as components endowed with anticorrosive or antiwear properties, surfactants, EP additives, etc depending on the specific use they are intended for.

20 The formulations of a few lubricating compositions according to the invention are indicated in the following examples, which are given for merely illustrative purposes. In Example 13 (Rolling and PSCT tests), alloys and mechanical characteristic thereof are disclosed eg in "Registration records of International alloy designation. Chemical Composition Limits for wrought aluminium and wrought alloy". Aluminium Association - Dusseldorf, Washington.

#### 25 Example 1

Composition:

23.0g of a monocarboxylic acid with perfluoropolyetheral structure belonging to class 1, having an average equivalent weight equal to 668,

30 - 7.8 ml of an ammonia aqueous solution at 10% by weight of ammonia;

- 53 ml of isopropyl alcohol;

- 384 ml of bidistilled water.

The sample contained 4.6% by weight of fluorinated substances and had a viscosity equal to 1.16 cst at 40 ° C and an almost neutral pH (product reference: LR.1).

35

#### Example 2

Composition:

40 - 9.4g of ammonium salt of the monocarboxylic acid with perfluoropolyetheral structure belonging to class 1, having an average equivalent weight equal to 636;

- 1.3 g of a monofunctional alcohol having perfluoropolyetheral structure belonging to class 1, having an average equivalent weight equal to 600;

- 0.2 g of triethanolamine sebacate dissolved in 4.2 g of normal-butyl alcohol;

45 - 2.7 g of the PFPE having perfluoropolyetheral end groups belonging to class 1 and having an average molecular weight equal to 650 ;

- 82.2 g of bidistilled water.

The resulting O/W microemulsion contained 13.5% by weight of fluorinated substances and contained 0.2% of triethanolamine sebacate (product reference: 6/87).

#### 50 Example 3

Composition:

- 17.17 g of a monocarboxylic acid with perfluoropolyetheral structure belonging to class 1, having an average equivalent weight equal to 441;

55 - 8.8 ml of an ammonia aqueous solution at 10% by weight of NH<sub>3</sub>;

- 284 ml of bidistilled water.

The solution contained 5.05% by weight of fluorinated substances and had a viscosity of 0.75 cst at 40 ° C; the pH was equal to 8.2 (product reference: LR.3).

Example 4

Composition:

- 150.4 g of a monocarboxylic acid with perfluoropolyetheral structure belonging to class 1, having an average equivalent weight equal to 443 and a narrow molecular weight distribution;
- 52.1 g of an ammonia solution at 10% by weight of ammonia;
- 10.8 g of a perfluoropolyether having an average molecular weight equal to about 1,200;
- 32.4 g of a fluorinated alcohol having a perfluoropolyetheral structure and a molecular weight equal to 678;
- 23.0 g of isopropyl alcohol;
- 293.1 ml of bidistilled water.

The resulting microemulsion contained 6.5% by weight of fluorinated substances and had a pH equal to 4.4 (product reference: LR.17).

15 Example 5

Composition:

- 18.39 g of a monocarboxylic acid having perfluoropolyetheral structure belonging to class 7, having a chlorofluoroalkyl end group for each molecule and having an average equivalent weight of about 850 and a wide distribution of the molecular weights;
- 6.44 g of an aqueous ammonia solution at 10% by weight of NH<sub>3</sub>;
- 338 g of bidistilled water.

The obtained solution contained 5.1% by weight of chlorofluorinated substances and had a pH equal to 8.3 (product reference: LR.15).

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Example 6

Composition:

- 19.8 g of a perfluoropolyether belonging to class 1 having carboxylic end groups and an average molecular weight equal to 4170;
- 14.6 g of isopropyl alcohol;
- 2.2 g of monocarboxylic acid having perfluoropolyetheral structure, belonging to class 1, having an average equivalent weight of 668;
- 63.4 g of aqueous phase containing the ammonia which is necessary to salify the carboxylic groups.

The O/W microemulsion obtained by mixing the above-listed components was a fluid, clear between 25 ° and 75 ° C, containing a viscosity of 38 cst at 40 ° C (product reference: LR.A).

Example 7

40 Composition:

- 5.3 g of a functionalized perfluoropolyether belonging to class 1, having carboxylic end groups and an average molecular weight equal to 2080;
- 19.2 g of isopropyl alcohol;
- 75.5 g of an aqueous solution containing the ammonia which is necessary to salify the carboxylic groups.

45 The O/W microemulsion obtained by mixing the abovesaid components was a fluid, limpid between 25 ° and 50 ° C, containing 5.3% by weight of fluorinated substances and having a viscosity of 2.25 cst at 40 ° C (product reference: LR.C).

Example 8

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Composition:

- 25.2 g of a monocarboxylic acid having perfluoropolyetheral structure, belonging to class 1, having an average equivalent weight equal to 668 and a wide distribution of the molecular weights;
- 9.1 ml of an aqueous ammonia solution at 10% by weight of ammonia;
- 1.4 ml of a perfluoropolyether having perfluoroalkyl end groups, belonging to class 1 and having an average molecular weight equal to 650;
- 28 ml of isopropanol;
- 280 ml of bidistilled water.

The sample was stable in the whole temperature range taken into examination, contained 8.2% by weight of fluorinated substances and had a viscosity of 1.2 cst at 40 °C, the pH being equal to 8 (product reference: LR.5).

5 Example 9

Composition:

- 55.0g of a monocarboxylic acid having perfluoropolyetheral structure belonging to class 7, having a chlorofluoroalkyl end group per molecule and having an average equivalent weight of about 478 and a wide molecular weight distribution;
- 10 - 62.14 g of triethanolamine;
- 10.14 g of bidistilled water.

The resulting solution contained 4.86% by weight of chlorofluorinated substances and had a pH equal to 8.36 (product reference: LR.15 TEA).

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Example 10

Composition:

- 26.18 g of ammonium salt of the acid belonging to class 1, having an average equivalent weight equal to 441;
- 20 - 1.4g of a perfluoropolyether of class 1, having perfluoroalkyl end groups and an average molecular weight of about 650;
- 5.6 ml of isopropyl alcohol;
- 293 ml of bidistilled water.

25 The system was limpid in the whole temperature range. It contained 8.8% by weight of fluorinated substances and had a viscosity of 0.85 cst at 40 °C; it was brought to a pH = 8 by adding thereto 0.15 ml of an ammonia solution at 10% by weight of ammonia (product reference: LR.7).

Example 11

30

Composition:

- 35.1 g of a monocarboxylic acid of perfluoropolyetheral structure belonging to class 1, having an average equivalent weight equal to 668 and a wide distribution of the molecular weights;
- 54 g of a monocarboxylic acid of perfluoropolyetheral structure belonging to class 1, having an average equivalent weight equal to 443 and a narrow distribution of the molecular weights;
- 35 - 11.3 g of ammonia solution at 10%;
- 2.8 g of a perfluoropolyether of class 1, having perfluoroalkyl end groups and an average molecular weight of about 1,200;
- 23.6 g of isopropyl alcohol;
- 40 - 300 ml of bidistilled water.

The microemulsion so obtained was stable in the whole temperature range. It contained 11.4% by weight of fluorinated substances and had a pH equal to 7.4. (Product reference: LR.9).

The following examples describe the preparation of additive-containing microemulsions.

45

Example 12

Composition:

- 50 - 108.0 g of a monocarboxylic acid with perfluoropolyetheral structure belonging to class 1, having an average equivalent weight equal to 668;
- 1.8 g of a monocarboxylic acid with perfluoropolyetheral structure belonging to class 1, having an average equivalent weight equal to 443 and a narrow distribution of the molecular weights;
- 33.7 g of ammonia solution at 10%;
- 55 - 33.4 g of perfluoropolyether having an average molecular weight of about 1,200;
- 23.6 g of a solution of triethanolamine sebacate in isopropanol, at 10.2% by weight;
- 3.1 g of isopropanol;
- 240 ml of bidistilled water.

The resulting O/W microemulsion contained 32.3% by weight of fluorinated substances and 0.6% by weight of triethanolamine sebacate, and had a pH equal to 7.6 (product reference: LR.10).

### Example 13

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90.3 g of the sample described in the preceding example 12 was diluted with 250 ml of water.

The resulting O/W microemulsion contained 8.6% by weight of fluorinated substances and 0.2% by weight of triethanolamine sebacate, the pH being equal to 5.3 (product reference: LR.11).

70 The utilization characteristics of the lubricating compositions according to the invention, with reference to specific applications, are illustrated in detailed hereinafter.

### Rolling

15 The lubricating compositions under examination were subjected to the "Plane Strain Compression Test" (paper 2015 by R.D. Guminski and J. Willis - Journal of the Institute of Metals, 1959-60, vol 88). The Plane Strain Compression Test is an improvement of the BISRA Compression Test (see The Rolling of Metals by L.R. Underwood, pages 116-119 - Chapman and Hall - London 1952) and is well indicative of the thickness reduction capacity of the lubricants in the cold-rolling of aluminium: the data determined in the plane strain

20 compression test are well in correlation to the behaviour in use exhibited by the lubricating mixtures. Further literature sources on the P.S.C.T., which extend the validity of the test also to steel, are : Kubie and Delamare - Journal of Lubrication Technology, pages 538-551 - 1982, vol 104).

25 The test carried out according to Guminski/Willis was the following : A 50x2.52x150 mm strip of aluminium alloy 3003 - H22 was subjected, after wetting with the lubricant, to 5 successive compressions between two vertical plates measuring 75x6.20 mm in a press mounted in a traction/compression machine, the whole in accordance with the indication given by Guminski and Willis, with the exception that the applied load was of 6,800 kg in order to make the test more selective.

The fluids of the present invention can be applied to the metal surface according to conventional methods such as immersion, spraying, and by means of jets, brushes, wiping, rollers or the like.

30 In the following examples, the composition was applied by brush. The results are reported in the following Table 1.

Table 1

35

Product	Thickness reduction (%)
Oil Lamium <sup>R</sup>	54
Example 1 (LR.1)	65
Example 2 (6/87)	67
Example 7 (LR.C)	60
Example 11 (LR.9)	62

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Lamium<sup>R</sup> is a rolling oil, which is usually utilized and is based on isoparaffin mineral oil with 5-6% of lauryl alcohol and minor amounts of fatty acids and of antioxidants (CRODA, U.K., BC21). Another typical known product is Somentor N. 35 produced by Esso, which gives equivalent results.

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Determination of the friction coefficient by means of the Plane Strain Compression Test (PSCT), as is described by Kubie and Delamare in the above-cited literature. Also this test, which provides the friction coefficient values, permits to evaluate the reduction ratios obtainable in the rolling process.

Metal test-piece (20x300 mm sheet thickness: about 0.6 mm), applied load: 10,000 kg:

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a) steel at 0.03% of C and 1% of Mn, annealed;

b) Al/Hg alloy 5052 0, annealed. The test-pieces were degreased by means of acetone before being tested.

Tested lubricants:

- a) composition of example 1 (LR.1);
- b) composition of example 5 (LR. 15);
- 5 c) composition example 7 (LR.C) ;
- d) composition of example 9 (LR. 15 TEA);
- e) rolling oil for the steel referred to as Q.27, a commercial product having the following composition:

70	- esters of nonylphenols + ethoxylated nonylphenols	3.95% by weight
	- antioxidant	0.50% by weight
	- antistain agent	5.00% by weight
	- animal fats	40.00% by weight
	- naphthenic mineral oil	50,00% by weight
15	- triethanolamine (TEA)	0.55% by weight

- f) emulsion of preceding product Q.27 at 10% by weight of water;
- g) palm oil;
- 20 h) product which is an aqueous emulsion at 4% by weight of the following oily composition:

25	- saturated acids C <sub>18</sub>	8.0% by weight
	- alcohols C <sub>8</sub> -C <sub>18</sub>	5.0% by weight
	- alcohols C <sub>16</sub> -C <sub>18</sub>	2.5% by weight
	- emulsifier	11.0% by weight
	- polyisobutane dissolved in C <sub>17</sub> /C <sub>18</sub> mixture	73.5% by weight

30 The tests on steel were carried out with a load corresponding to a thickness reduction of about 30%; the tests on Al alloy were conducted at a pressure corresponding to a thickness reduction of about 60%. The results are indicated in Tables 2 and 3.

Table 2

(PSCT test on steel)											
OUR REF.	EX. NO.	$\bar{\mu}$									
		N = 1	N = 2	N = 3	N = 4	N = 5	N = 6	N = 7	N = 8	N = 9	N = 10
LRI	1	0.03	0.028	0.034	0.045	0.04	0.042	0.04	0.045	0.05	0.045
LRI 15	5	0.025	0.032	0.03	0.04	0.045	0.035	0.04	0.045	0.05	0.042
45 L.R. 15 TEA	9	0.048	0.048	0.042	0.048	0.05	0.053	0.38	0.04	0.048	0.052
LRC	7	0.042	0.03	0.032	0.03	0.04	0.038	0.04	0.045	0.045	0.045
Q.27		0.052	0.052	0.052	0.065	0.062	0.060	0.060	0.065	0.065	0.07
Q.27 10%		0.072	0.068	0.069	0.070	0.070	0.071	0.065	0.071	0.068	0.072
50 Palm oil (non emuls.)		0.057	0.057	0.060	0.058	0.060	0.060	0.060	0.065	0.065	0.060
$\bar{\mu}$ = Tresca friction coefficient N = number of indentations											

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TABLE 3

(PSCT results on annealed ALUMINIUM 5052)												
OUR REF.	FLUID	NUMBER OF EX. PREP.	$\bar{\mu}$									
			N = 1	N = 2	N = 3	N = 4	N = 5	N = 6	N = 7	N = 8	N = 9	N = 10
LR.15	CIR <sub>7</sub> COONH <sub>4</sub> solution	9	.051	.05	.050	.051	.052	.051	.051	.052	.055	.056
TEA		5	.062	.058	.058	.058	.058	.057	.058	.058	.058	.059
LR.15	CIR <sub>7</sub> COONH <sub>4</sub> solution											
LR.1	Galden solution of salified acid (PE 668)	1	.054	.053	.049	.049	.049	.05	.050	.050	.052	.054
T.5263	hydrocarbon emulsion	Product according to the art	.175	.148	.084	.068	.070	.060	.058	.057	.054	.058

$\mu$  = Coulomb friction coefficient  
N = number of indentations

### Dishing

Dishing is the process by means of which a metal plate is subjected to permanent plastic deformation by buckling between two surfaces (die and punch).

The lubricant must have good EP characteristics (high pressures), i.e. it must secure the sliding between two metal surfaces (sheet iron to be deformed and dies) under a high pressure, and that is achieved by lubricants which do not exhibit any film rupture under such conditions. In general different lubricants are utilized at present, depending on the type of dishing to be carried out and on the materials to be worked; the lubricants may be a mineral oil with various additives, as well as soap baths, emulsions, waxes, greases, fluoride and phosphate baths, chloroparaffins, polymeric resins, graphite or MoS<sub>2</sub> in oil etc.

The PFPE-based aqueous compositions according to the present invention are suited also as lubricants for the dishing process.

The use of these compositions in this type of application is novel. The compositions are suited to the dishing of metals as they permit a dishing ratio comparable to the ones obtainable with whole oils based on hydrocarbons, while remarkably reducing the necessity to degrease the sheets for the subsequent processing steps.

The compositions of the invention may further contain minor amounts of additives for particular operative conditions if necessary. Such additives may be for instance corrosion inhibitors, antistatic agents, surfactants or slippage agents.

### Examples

The fluids of the invention were subjected to the Erichsen test (UN 8341) on steel PE PO4, (UNI).

The fluids of the present invention are applicable to the metal surface by means of conventional methods such as dipping, spraying, wiping, by brushes, roller or the like. The results, which are reported on the following table 4, indicate the depth of penetration, in tenths of mm, of the punch into a sheet-steel having a roughness of 0.8 microns.

Table 4

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10

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Erichsen values	
	test-piece 1
in dry conditions	116.3±0.5
standard oil (*) Metalform <sup>R</sup>	126.7±1
LR 5 (example 8)	124-123.7±0.7
LR A (example 6)	126.7±0.5
LR C (example 7)	124-15.7±1.5

(\*) The oils for dishing usually utilized at present are based on mineral oil and additioned fatty acids (antioxidants etc.).

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Lubricating properties of the fluids according to the invention

For the fluids utilized in several plastic processings of metals, good EP characteristics may be required. In order to determine the EP characteristics of the microemulsions and aqueous solutions of per-fluoropolyethers and derivatives thereof, "Shell 4 balls" tests (IP 239/79) were carried out. The "Shell 4 balls" tests were always carried out using balls made of steel UNI 100 Cr<sub>6</sub>.

25

Examples

The fluids according to the invention were subjected to the "Shell 4 balls" test (IP 239/79 ASTM D2783). The results are indicated in the following table.

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T a b l e

5	E x.	ref.	seizure		welding	average load
			beginning test			
			10	%(**)	(Kg)	(Kg)
	1	LR1	4,6	178	178	55
15	3	LR3	5	89	282	78
	5	LR15	5,1	200	224	70
	6	LRA	22	100	178	48
20	7	LRC	5,3	251	251	87
	8	LR5	8,2	126	178	56
25	10	LR7	8,8	100	251	71
	11	LR9	11	178	178	56
30	14	LR17	6,5	251	251	79
	12	LR10	32,6	178	178	58
35	13	LR11	8,6	178	178	62
	19	LR15TEA	4,86	251	316	98
40	(*)	O.C.E.	6	158	178	60
		O.C.E.	10	178	178	61

45 (\*) Commercial, highly additioned emulsifiable oil composed  
of : 50% of mineral oil, 3% of chlorinated paraffin,  
50 4% of non-ionic emulsifier, 1% of antistain agent,  
0.5% of biocide, 40% of animal fat oils, 0.5% of anti-  
55 fcaming agent, 1% of corrosion inhibitors and other

agents.

5 (\*\*) % by weight of product in the aqueous emulsion.

The reported data show that the compositions according to  
 10 the invention possess satisfactory properties in EP cond-  
 itions also without additives, these properties being comp-  
 15 arable with those of commercial products containing a high  
 amount of specific additives.

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**Claims**

1. A metal processing composition which is an aqueous composition characterised by containing from 1  
 25 to 40% by weight of a perfluoropolyetheral compound having an average molecular weight of at least 400  
 with end groups of the perfluoropolyetheral chain consisting of perfluoroalkyls and/or of functional groups.

2. A composition according to claim 1 in which the perfluoropolyether has carboxylic end groups which  
 are salified, preferably with ammonia or triethanolamine.

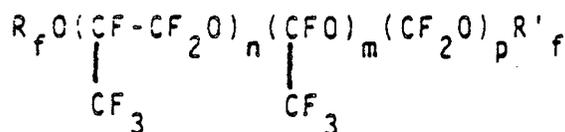
3. A composition according to claim 1 or claim 2 which is in the form of a microemulsion.

30 4. A composition according to any preceding claim in which the the perfluoropolyether has an average  
 molecular weight in the range from 400 to 5,000, preferably 600 to 2,000.

5. A method according to claim 1 in which the perfluoropolyether is selected from the following classes:

1)

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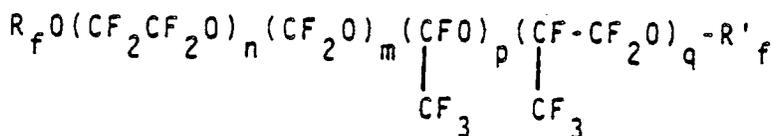
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with a random distribution of the perfluorooxyalkylene units, wherein R<sub>f</sub> and R'<sub>f</sub> like or different from each  
 other, are -CF<sub>3</sub>-, -C<sub>2</sub>F<sub>5</sub>-, -C<sub>3</sub>F<sub>7</sub>-, or -COOH, -CF<sub>2</sub>COOH, and m, n, p have such values as to meet the  
 aforesaid average molecular weight requirements;

45 2) R<sub>f</sub>O(CF<sub>2</sub>CF<sub>2</sub>O)<sub>n</sub>(CF<sub>2</sub>O)<sub>m</sub>R'<sub>f</sub>, with a random distribution of the perfluorooxyalkylene units, wherein R<sub>f</sub>  
 and R'<sub>f</sub>, like or different from each other, are -CF<sub>3</sub> or -C<sub>2</sub>F<sub>5</sub>-, or -COOH, -CF<sub>2</sub>COOH and m and n have such  
 values as to meet the abovesaid requirements;

3)

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with a random distribution of the perfluorooxyalkylene units, wherein R<sub>f</sub> and R'<sub>f</sub>, like or different from each  
 other, are -CF<sub>3</sub>-, -C<sub>2</sub>F<sub>5</sub> or -C<sub>3</sub>F<sub>7</sub>-, or one of the above-indicated carboxylic radicals, and m, n, p, q have such

values as to meet the abovesaid requirements;

4)

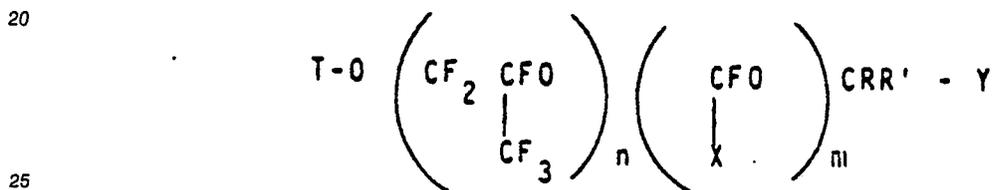


10 wherein  $R_f$  or  $R'_f$ , like or different from each other, are  $-C_2F_5$  or  $-C_3F_7$  or one of the above-indicated carboxylic radicals, and  $n$  has such a value as to meet the abovesaid requirements;

5)  $R_f O (CF_2 CF_2 O)_n R'_f$  wherein  $R_f$  and  $R'_f$ , like or different from each other, are  $-CF_3$ ,  $-C_2F_5$ , or one of the above-indicated carboxylic radicals, and  $n$  has such a value as to meet the abovesaid requirements;

15 6)  $R_f O (CX_2 CF_2 CF_2 O)_n R'_f$  wherein  $R_f$  and  $R'_f$ , like or different from each other, are  $-CF_3$  or  $-C_2F_5$  or  $-C_3F_7$  or one of the above-indicated carboxylic radicals,  $X$  is  $F$  or  $H$ ,  $n$  having such a value as to meet the abovesaid requirements;

7)



wherein  $X$  is  $F$  or  $CF_3$ ,  $R$  is  $F$  or  $Cl$  or  $Br$  or  $I$ ,  $R'$ , like or different from  $R$ , is also  $F$  or  $Cl$  or  $Br$  or  $I$ ,  $Y$  is a  $-COOH$  group or a perfluoroalkyl group,

30  $T$  is a perfluoroalkyl group containing one or two atoms of  $Cl$  or  $Br$  or  $I$ ; in particular it may be  $\text{Alog } CF_2-$ ,  $\text{Alog } CF_2 CF-$

where  $\text{Alog}$  is  $Cl$  or  $Br$  or  $I$ ,

$n$  ranges from 1 to 15, the  $m/n$  ratio ranging from 0.01 to 0.5.

35 6. Use of perfluoropolyetheral compound having an average molecular weight of at least 400 with end groups of the perfluoropolyetheral chain consisting of perfluoroalkyls and/or of functional groups in an aqueous composition which is a lubricating/refrigerating liquid in the cold plastic processing of metals.

7. Use according to claim 6 in which the processing includes rolling, dishing and/or drawing.

8. Use according to claim 6 or 7 in which the composition is as defined in any of claims 2 to 5.

40 9. A process for treatment of metals by cold plastic processing using an aqueous lubricating/refrigerating composition characterised in that the composition contains from 1 to 40% by weight of a perfluoropolyetheral compound having an average molecular weight of at least 400 with end groups of the perfluoropolyetheral chain consisting of perfluoroalkyls and/or of functional groups.

10. A process according to claim 9 in which the composition is as defined in any of claims 2 to 5.

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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.5)
D,X	EP-A-0 250 766 (AUSIMONT) * Claims 1-5; page 14, column 2 * ---	1-10	C 10 M 173/02 // C 10 N 40/20 C 10 N 40/24
D,X	J. AM. CHEM. SOC., vol. 107, no. 5, 1985, pages 1197-2101; D.F. PERSICO et al.: "Synthesis of perfluoropolyethers via hydrocarbon polysters: A new general method" * Page 1201, column 1, paragraph 2 - column 2, paragraph 3 * -----	1-10	(C 10 M 173/02 C 10 M 147:04 )
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-10-1989	Examiner RO TSAERT L.D.C.
<b>CATEGORY OF CITED DOCUMENTS</b> 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	