



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/US91/09064 (22) International Filing Date: 10 December 1991 (10.12.91) (30) Priority data: 626,607 12 December 1990 (12.12.90) US 626,499 12 December 1990 (12.12.90) US 626,500 12 December 1990 (12.12.90) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: TANNENBAUM, Harvey, Paul ; 9 Overbrook Parkway, Wynnewood, PA 19096 (US). (74) Agents: BURGESS, Richard, H. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent), SU ⁺ . Published <i>With international search report.</i>
(54) Title: NON-STICK COATING SYSTEM WITH PTFE OF DIFFERENT MELT VISCOSITIES FOR CONCENTRATION GRADIENT (57) Abstract Improved non-stick coating systems can be applied to untreated smooth substrate with a primer of a first polytetrafluoroethylene having a melt viscosity over 10⁵ Pa Sec plus a second polytetrafluoroethylene having a melt viscosity in the range of 10² to 10⁷ Pa Sec, with the melt viscosity of the first being at least 10² Pa Sec higher than that of the second to give a concentration gradient.		

+ DESIGNATIONS OF "SU"

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TITLE

NON-STICK COATING SYSTEM
WITH PTFE OF DIFFERENT MELT
VISCOSITIES FOR CONCENTRATION GRADIENT
BACKGROUND OF THE INVENTION

5 This invention relates to coatings systems, such as for cookware, which minimize sticking. More particularly, it relates to multilayer coating systems that can be used directly on smooth, untreated substrates and which provide concentration gradients within the coating.

Generally in the art a metal or glass substrate is roughened by
10 some means before the first layer of coating is applied so that mechanical bonding will assist chemical adhesive means in holding the coating onto the substrate. Typical roughening means include acid etching, sand-blasting, grit-blasting, and baking a rough layer of glass, ceramic or enamel frit onto the substrate. The problem of adhesion of non-stick coatings to substrates is
15 exacerbated by the nature of the coatings. If the coating is optimized for release to prevent food particles from sticking to it, for easy clean-up after cooking or durability, or to facilitate low friction sliding contact, almost by definition there will be difficulties in making it adhere well to the substrate.

The substrate can be metal, often aluminum or stainless steel
20 used for cookware or industrial applications. It can be glass or ceramic. It might even be plastic for microwave oven cookware, or it could be an industrial article such as a saw made of carbon steel. Whatever the substrate or the application, if it is necessary to roughen the substrate to make the coating adhere, that at least adds cost and can cause other difficulties
25 including creating a rough profile which can protrude or telegraph through the coating. This is especially undesirable when smoothness is sought, such as for saws, steam irons and copier rolls. The environmental cost of disposing of etchant materials can be significant. Sometimes, especially for glass and ceramic substrates, it also can cause unacceptable weakness or
30 brittleness of the substrate.

Means of enhancing adhesion of non-stick coatings to a substrate are illustrated by the following patents.

U.S. 4,049,863 - Vassiliou (1977) teaches a primer containing fluoropolymer, such as polytetrafluoroethylene (PTFE), colloidal silica and a

polyamide imide (PAI), along with other constituents, applied by various techniques to a substrate that is preferably pretreated by grit blasting, flame spraying of metals or metal oxides or frit coating, or to phosphated and chromated metals. The PTFE:PAI ratio can be 1:9. The primer coat is ordinarily applied to a dry film thickness (DFT) of about 2-15 microns (μm). After air drying, the primer is topcoated with a conventional fluoropolymer enamel and baked. (Parts, percentages and proportions herein are by weight except where indicated otherwise.)

U.S. 4,087,394 - Concannon (1987) discloses aqueous concentration gradient coatings of fluoropolymer which is 20-80% of a homopolymer or a copolymer of fluorinated ethylene-propylene (FEP) made of 5-100% tetrafluoroethylene (TFE) with 95-0% hexafluoropropylene (HFP), with 80-20% of a film forming polymer which can be PAI. The coating is applied by spraying onto aluminum sheet, or a variety of substrates. Other application techniques are mentioned. Nothing is said about substrate preparation. Although PTFE and FEP are treated as a continuum, there are no suggestions to use a blend such as 50% PTFE, 50% FEP.

U.S. 3,928,675 and 3,857,852, both to Tieszen, teach the use of high viscosity ($> 10^{10}$) and low viscosity (10^4 poise) (10^9 and 10^3 Pa Sec) PTFE along with polyarylene sulfide such as polyphenylene sulfide (PPS) in coatings.

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SUMMARY OF THE INVENTION

The present invention, in certain of its embodiments, provides a coating composition comprising perfluorocarbon resin and at least one of polyamide imide and polyether sulfone resins, wherein the perfluorocarbon resin comprises at least two different polytetrafluoroethylene resins, the first having a melt viscosity of at least 10^6 poises (10^5 Pa Sec), and the second having a melt viscosity in the range of 10^3 to 10^8 poises (10^2 to 10^7 Pa Sec), with the melt viscosity of the first being at least 10^2 poises (Pa Sec) higher than that of the second.

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The invention also comprises multi-layer coating systems on substrates with the defined coating composition in the primer or in the topcoat.

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DETAILED DESCRIPTION

The present invention permits not only lower cost by avoiding the roughening of the substrate but also smoother coated surfaces which can be advantageous for release on cookware, and for the gliding effect on steam iron sole plates. Also it can allow elimination of costly polishing of coated copier roll surfaces and application of dispersion PTFE coatings by coil
5 coating and roller coating techniques.

Various embodiments of the invention involve using at least two PTFE resins having different melt viscosities in a primer or a topcoat. One pair of resins has relatively high and low melt viscosity resins. Another has relatively low and lower still melt viscosity resin.

10 The adhesion of high melt viscosity fluoropolymer coatings to all types of metal substrates, particularly to smooth metal, can be significantly improved through chemically induced stratification or formation of a concentration gradient in the primer.

Addition of perfluorocarbon polymer having a low melt
15 viscosity (MV) in the range of 10^3 - 10^8 poise (10^2 - 10^7 Pa Sec), to a primer system composed of PTFE with a high MV of 10^{11} poise (10^{10} Pa Sec) and a polymeric binder such as polyamide-imide or polyphenylene sulfide, imparts a synergistic effect in which the fluoropolymer stratifies away from the substrate interface allowing the polymeric binder to obtain a higher
20 concentration and degree of cure at the substrate interface resulting in improved adhesion. The required cure temperature to achieve this stratification can be modified by the choice of fluoropolymer.

Melt viscosity of perfluoropolymers can be determined by know technique such as that in U.S. Patent 4,636,549 - Gangal et al (1987).
25 See Col. 4, lines 25 - 63.

With use of the coatings of the invention on smooth substrates, treated only by washing to remove grease and any other contaminants which might interfere with adhesion, coating systems of the invention give good food release and good resistance to usual durability tests
30 such as the "tiger paw" abuse cooking tests involving a weighted holder with multiple ball point pen shafts rotating around the inside of a frying pan during cooking tests. The tests are generally described in U.S. patent 4,252,859, -- Concannon and Vary (1981) col. 2, lines 14-24.

Typical prior art preparation of surfaces to enhance adhesion of a release coating has involved etching or sand or grit blasting to develop a surface profile. The profile is measured in average microinches using a model RT 60 surface roughness tester made by Alpa Co. of Milan, Italy. The profile on typical rolled aluminum after washing to remove grease and contaminants is 16-24 microinches (.6 - 0.96 μm). The profile on steel varies 5 more widely but is typically less than 50 microinches (2 μm). On both steel and aluminum, before a release coating is applied the profile typically is increased to over 100 micro inches (4 μm), preferably for aluminum for some uses to 180-220 micro inches (7.2 - 8.8 μm). Thus, the present invention is particularly useful with steel or aluminum substrates having a profile of less 10 than 100, preferably less than 50 micro inches (less than 4 μm , preferably less than 2 μm).

Similar effects can be achieved using a low MV (at least 10^6 10^5 Pa Sec) PTFE with a lower still MV (10^3 to 10^5 poise or 10^2 to 10^4 M Pa Sec) PTFE. To obtain stratification, it is desirable to have a difference of at 15 least 10^2 poise in melt viscosities of the two PTFE's.

The primers of the invention can also be used on substrates roughened in various ways known in the art to make coating systems even better than without such undercoats. This can combine improved chemical adhesion with mechanical effects to produce products that may be superior.

20 In the following examples, the polyamide imide, colloidal silica and dispersions are known in the art and preferably are those of U.S. Patent 4,049,863 - Vassiliou (1977); and the ultramarine blue is that of U.S. Patent 4,425,448 - Concannon and Rummel (1984).

The following examples and test data demonstrate this 25 improved adhesion when used as a primer for fluoropolymer topcoats. The fluoropolymers are provided as 60% dispersions in water. As usual, the solids content of dispersions is indicated in the tables. The compositions were blended by techniques normal in the art and then applied to a smooth, degreased aluminum substrate by spraying.

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EXAMPLE 1: Polymerization and Concentration
of Lower MV PTFE

A cylindrical, horizontally disposed, water jacketed, stirred, stainless steel reactor having a length to diameter ratio of about 1:5, a 4-bladed cage-type agitator running the length of the reactor, and a water capacity of about 80 parts was charged with 46 parts of demineralized water and 0.022 parts of ammonium perfluorocaprylate dispersing agent. The reactor was pressure tested at 2.8 MPa and 90° C while stirring the reactor contents at 46 rpm. The reactor was then cooled to reduce the temperature of its contents below 30° C. The reactor was then evacuated and purged three times with tetrafluoroethylene (TFE) monomer, leaving a reduced pressure on the reactor after the final evacuation. A valve was then opened to slowly release ethane into the reactor until the pressure was raised by 0.06 MPa. The valve was then closed and the reactor temperature was raised to 90° C with the agitator running at 46 rpm. After the temperature reached 90° C, the reactor was pressurized with TFE to a pressure of 2.6 MPa. A freshly prepared solution of 1.1 parts of a solution of (0.1%) ammonium persulfate (APS) and (1.5%) disuccinic acid peroxide (DSP) in demineralized water was pumped into the reactor at a rate of 0.11 parts/minute to initiate polymerization. After polymerization began (0.07 MPa drop in reactor pressure), additional TFE was added to the reactor at a rate so as to maintain the pressure at 2.6 MPa. After 3 parts of TFE had been added to the reactor after kickoff, 2.2 parts of a 2.4% solution of ammonium perfluorocaprylate in demineralized water was pumped into the reactor at a rate of 0.2 parts/minute. After 15 parts TFE addition, 0.66 parts of a solution of APS (0.05%), DSP (0.5%), and methanol (0.5%) in demineralized water were pumped into the reactor at a rate of 0.11 parts/minute. When 22 parts of TFE had been added to the reactor, the TFE feed was stopped but the reaction was continued until the reactor pressure dropped to 1.3 MPa. The reactor was then vented and the product dispersion was removed. The dispersion contained about 34% polymer by weight. A small amount of the dispersion was coagulated by the application of vigorous stirring and the resulting powder was then dried in a 120° C oven.

The melt viscosity of the dried resin was measured at 372° C by the procedure described in ASTM D-1238-52T modified by (1) using a

cylinder, orifice, and piston tip made of a corrosion-resistant alloy, Haynes Stellite 19, (2) charging a 5.0 g sample to the 9.53 mm ID cylinder, and (3) five minutes after charging, the sample is extruded through a 2.10 mm diameter, 8.00 mm long square-edged orifice under a load of 5000 g. The melt viscosity in poise was calculated as 36,910 divided by the observed extrusion rate expressed in grams per minute. The melt viscosity of this dried powder was 5.6×10^4 poise (5.6×10^3 Pa Sec).

The remaining as-polymerized dispersion was heated to 80° C while gently stirring. When the temperature reached 40-45° C, a weight of Triton X-100 non-ionic surfactant of octyl phenol polyether alcohol sold by Rohm and Haas Co. equivalent to 8% of the weight of polymer was added to the dispersion. Citric Acid (0.02% based on polymer) and then 19% aqueous ammonium carbonate solution (0.7% based on polymer) were then added. When the temperature reached 80° C, the agitation and heat were stopped. Upon cooling, the dispersion separated into two layers with nearly all of the polymer being concentrated in the lower layer. This lower layer was removed and analyzed for % solids and % Triton X-100. The respective levels were found to be 53.6% solids and 3.7% Triton X-100. Adjustments were made with water and Triton X-100 additions so that the final levels were 46.7% and 8.9% respectively.

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EXAMPLE 2: Polymerization and Concentration of Higher MV PTFE

A batch was polymerized in a similar manner to that described in Example 1 except for the following; (1) the precharge included 1.3 lbs. of paraffin wax, and (2) chloroform (0.026 parts) was added to the reactor in place of ethane. All other respects of the polymerization were identical to that described in Example 1. The product dispersion contained 34% (by 5 weight) polymer.

A small amount of the dispersion was coagulated and dried. The melt viscosity of the dried powder was measured as above except that the 5000 g weight was replaced by a 15,000 g weight. The melt viscosity was then calculated by dividing 110,250 by the observed melt flow in grams per 10 minute. The value obtained was 7.3×10^6 poise.

The remaining dispersion was concentrated in an identical manner to that described above except that the ammonium carbonate solution was replaced by an equivalent amount of 28% ammonium carbonate solution. The final solids level was 60.2% and the Triton X-100 level was 5.9%.

15 Low MV PTFE for the invention can be provided in the form of as-polymerized micropowder made in accordance with this example or in the form of irradiated and comminuted micropowder made by techniques such as taught by the above-identified Brown et al and Derbyshire patents.

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EXAMPLE 3: Low MV PTFE/Regular PTFE - Multiple Coat System

Composition:

Table 1

Weight Percent	
5	0.008 Zinc oxide
	0.050 "Afflair 153" titania coated mica from EM Industries
	6.701 Ultramarine blue pigment
10	6.966 "T-30" PTFE from Du Pont
	1.002 "Ludox AM" colloidal silica from Du Pont
	4.760 L171 PTFE micropowder from ICI
	4.790 AI-10 polyamide imide resin from Amoco
	66.319 Deionized water
15	0.455 "Triton X-100" octyl phenol polyether alcohol non-ionic surfactant from Rohm and Haas
	0.676 Diethylethanolamine
	1.352 Triethylamine
	3.728 Furfuryl alcohol
	<u>3.193</u> N-methyl pyrrolidone
20	100.000 TOTAL

Application:

This system is comprised of a primer of the invention which is applied at 5-10 μm dry film thickness (DFT) to a metal surface which has been washed to remove oil and dirt contamination, air dried, and topcoated with a single (15-17.5 μm DFT) or multiple topcoats in thicknesses of 12.5-17.5 μm DFT each and having compositions similar to those shown in the Table 1. The films are baked 10 minutes at 150° C followed by a high temperature bake for a minimum of 3 minutes over 415° C.

Two different proportions of resins were used as a primer with a topcoat on smooth aluminum cookware which was subjected to tiger paw testing, described above. The number of standard cooking cycles to a rating of 5, determined by coating deterioration, was recorded and presented below along with the percentages of the comparable value for a commercial coating

on a grit-blasted substrate run as a control. The results are better than many good commercial products.

Testing:

Table 2

Cooking Performance of Low MV PTFE/PTFE Primer

<u>Low MV/Regular PTFE</u>				<u>Cooks to Rating of 5</u>	
				% of	
<u>System</u>	<u>Surface</u>	<u>DFT</u>	<u>Range</u>	<u>Average</u>	<u>Commercial</u>
40/60	Smooth	1.0-1.1	55-70	62	103
30/70	Smooth	1.0-1.1	55-60	60	100

Low MV PTFE for the invention can be provided in the form of as-polymerized micropowder made in accordance with Example 1 or in the form of irradiated and comminuted or ground micropowder made by known techniques.

A preferred topcoat is that of Example 1 of U.S. Patent 4,118,537. Alternatively, the coats above the undercoat and primer (topcoat and optional intermediate coats) can be those of U.S. Patent 4,252,854; 4,351,882; and 4,425,448, and combinations thereof.

EXAMPLE 4: Single Coat

Unique Coating Characteristics:

This coating is unique in that one can obtain excellent adhesion to smooth metal at fluoropolymer to binder ratios of up to 10:1. It produces a high gloss appearance and a silky feel in a one-coat. The two types of PTFE were made in accordance with Examples 1 and 2.

Composition:

Table 1

Low MV PTFE Single Coat

Weight

Percent

5	2.080	"Afflair 153" titania coated mica from EM Industries
	1.984	Channel black pigment
	0.992	Aluminum silicate
10	14.664	PTFE MV = 7.3×10^6 poise (7.3×10^5 Pa Sec)
	3.489	"Ludox AM" colloidal silica from Du Pont
	11.742	PTFE MV = 5.6×10^4 poise (5.6×10^3 Pa Sec)
	3.394	AI-10 polyamide imide resin from Amoco
	0.138	Sodium polynaphthalene sulfonate
	53.352	Deionized water
15	1.784	"Triton X-100" octyl phenol polyether alcohol non-ionic surfactant from Rohm and Haas
	0.479	Diethylethanolamine
	0.958	Triethylamine
	2.607	Furfuryl alcohol
	2.263	N-methyl pyrrolidone
20	<u>0.074</u>	Triethanol amine
	100.00	TOTAL

Application:

Applied at 17.5-20 μ m dry film thickness (DFT) to degreased metal and cured for 10 minutes at 150° C followed by 3 minutes at 427° C.

25 Testing:

This coating passes fingernail adhesion and crosshatch testing both prior to and after boiling in water for 15 minutes.

Low MV PTFE for the invention can be provided in the form of as-polymerized micropowder made in accordance with Example 1 or in
30 the form of irradiated and comminuted micropowder.

If, instead of using the coatings of the invention as a single coat, it is desired to use them as primers, then a preferred topcoat is that of Example 1 of U.S. Patent 4,118,537. Alternatively, the coats above the

undercoat and primer (topcoat and optional intermediate coats) can be those of U.S. Patent 4,252,854; 4,351,882; and 4,425,448, and combinations thereof.

EXAMPLE 5: Topcoat

		<u>Table 2</u>	
	INGREDIENT	TOPCOAT 1	TOPCOAT 2
5	"T-30" PTFE from Du Pont	280.74	196.52
	PTFE MV = 5.6×10^4 poises (5.6×10^3 Pa Sec) from Example 1	16.85	101.07
10	"Afflair 153" titania-coated mica from EM Industries	0.42	0.42
	Organic Liquids		
	Butyl Carbitol	9.67	(ditto
	Hydrocarbon Solvent	11.95	Topcoat 1)
15	Cerium Octate	2.25	
	Triethanol Amine	18.52	
	Oleic Acid	4.95	
	Triton X-100	2.45	
	Total Organic Liquids	50.01	50.01
20	Acrylic Latex of 39 parts by weight terpolymer of methyl methacrylate/57 parts ethyl acrylate/4 parts methacrylic acid, dispersion		
25	at 40% solids in water, 0.2 μ m average particle size	52.12	52.12
	Carbon black mill base	5.99	5.99
	Ultramarine blue mill base	1.34	1.34
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Application:

This system is comprised of a primer of PTFE, FEP and

polyamide imide of Example 1 which is applied at 5-10 μm dry film thickness (DFT) to a metal surface which has been washed to remove oil and dirt contamination, air dried, and topcoated with a single (15-17.5 μm DFT) or multiple topcoats of this example in thicknesses 12.5-17.5 μm DFT each and having compositions similar to those shown in Table 2. The films are baked 10 minutes at 150° C followed by a high temperature bake for a minimum of 5 3 minutes over 415° C.

EXAMPLE 6: Testing

Smooth aluminum bakeware with cupcake-shaped depressions were coated with primer of Example 4 and topcoat of Example 5. A variety 10 of types of baked goods were baked, then the bakeware was turned upside down. If the baked goods fell out easily, leaving no residue, the coating was rated best. Increasing amounts of residue sticking to the coating, and the need to hit the back of the bakeware or even to dig the baked goods out with a tool, gave progressively lower ratings. Trials were made on bakeware with 15 and without cooking grease applied between bakes.

The results without grease were equivalent to commercial coatings, and with grease were superior to commercial coatings.

For use with the topcoats of the invention, primers can be applied direct to smooth, degreased substrates, or the substrates can be grit- 20 blasted or etched to provide a greater profile, or frits can be applied first to the substrates.

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CLAIMS

1. An aqueous coating composition comprising perfluorocarbon resin and at least one of polyamide imide and polyether sulfone resins, wherein the perfluorocarbon resin comprises at least two different polytetrafluoroethylene resins, the first having a melt viscosity of at least 10^5 Pa Sec and the second having a melt viscosity in the range of 10^2 to 10^7 Pa Sec, with the melt viscosity of the first being at least 10^2 Pa Sec higher than that of the second.
2. The coating composition of claim 1 wherein the melt viscosity of said first resin is at least 10^{10} Pa Sec and of said second resin is in the range of 10^3 - 10^5 Pa Sec.
3. The coating composition of claim 1 wherein the melt viscosity of said first resin is at least 10^5 M Pa Sec and of said second resin is in the range of 10^2 - 10^4 Pa Sec.
4. The coating composition of Claim 1 wherein the perfluorocarbon resin contains, by weight, about 50-90% of said first resin, and 50-10% of said second resin.
5. The coating composition of Claim 2 consisting essentially of, by weight, about 3-5% colloidal silica, 1-4% surfactant, 15-30% polyamide imide resin, and 25-55% perfluorocarbon resin and the perfluorocarbon resin consists essentially of 60-85% of said first resin, the balance said second resin.
6. A coated substrate wherein the coating comprises a coating composition of Claim 1 and the substrate is free of contaminants that would prevent adhesion of the coating.
7. The coated substrate of claim 6 wherein the coating is a multi-layer non-stick coating comprising a primer, a topcoat and up to one or more intermediate coats between the primer and the topcoat.
8. The coated substrate of claim 7 wherein the primer is said coating composition.
9. The coated substrate of claim 7 wherein the topcoat is said coating composition.

10. The coated substrate of Claim 11 wherein the substrate is metal selected from aluminum, stainless steel and carbon steel which, before coating has a surface roughness profile less than $2 - 5 \mu\text{m}$.

11. The coated substrate of Claim 8 wherein the primer coating resulting from said aqueous dispersion is not uniform in composition throughout its thickness but has a lower concentration of said first 5 polytetrafluoroethylene at the interface with the substrate than at the opposite interface.

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/09064

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 09 D 127/18//, (C 09 D 127/18, C 09 D 179:08, C 09 D 181:06)											
II. FIELDS SEARCHED Minimum Documentation Searched ⁷ Classification System Classification Symbols IPC⁵ : C 09 D 127/00, C 09 D 179/00, C 09 D 181/00 Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸											
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <thead> <tr> <th style="width: 10%;">Category ¹⁰</th> <th style="width: 70%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;"> US, A, 4 548 986 (SUZUKI et al.) 22 October 1985 (22.10.85), see claims; examples. --- </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="padding: 5px;"> US, A, 4 167 605 (ATTWOOD et al.) 11 September 1979 (11.09.79), see claims; examples. ----- </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1</td> </tr> </tbody> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	X	US, A, 4 548 986 (SUZUKI et al.) 22 October 1985 (22.10.85), see claims; examples. ---	1	A	US, A, 4 167 605 (ATTWOOD et al.) 11 September 1979 (11.09.79), see claims; examples. -----	1
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¹⁰ Special categories of cited documents: ¹⁴ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family									
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <tr> <td style="width: 50%; padding: 5px; vertical-align: top;"> Date of the Actual Completion of the International Search 02 April 1992 </td> <td style="width: 50%; padding: 5px; vertical-align: top;"> Date of Mailing of this International Search Report 10. 04. 92 </td> </tr> <tr> <td style="width: 50%; padding: 5px; vertical-align: top;"> International Searching Authority EUROPEAN PATENT OFFICE </td> <td style="width: 50%; padding: 5px; vertical-align: top;"> Signature of Authorized Officer MORTENSEN </td> </tr> </table>			Date of the Actual Completion of the International Search 02 April 1992	Date of Mailing of this International Search Report 10. 04. 92	International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer MORTENSEN					
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ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

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to the International Search
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