# **PCT**

(22) International Filing Date:

08/545,441

# WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



### INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| (51) International Patent Classification •: | nt Classification o: |         | (11) International Publication Number:   | WO 96/30581               |  |
|---------------------------------------------|----------------------|---------|------------------------------------------|---------------------------|--|
| D06F 43/00                                  |                      | A1      | (43) International Publication Date:     | 3 October 1996 (03.10.96) |  |
| (21) International Application Number:      | PCT/US9              | 96/0288 | 86 (81) Designated States: BR, CA, CN, I | FI, JP, MX, NO, European  |  |

(30) Priority Data: 08/413,332 30 March 1995 (30.03.95)

30 March 1995 (30.03.95) US 17 October 1995 (17.10.95) US

4 March 1996 (04.03.96)

(71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventor: DAVIS, Maxwell, Gregory; 10583 Clemsford Road, Forest Park, OH 45240 (US).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

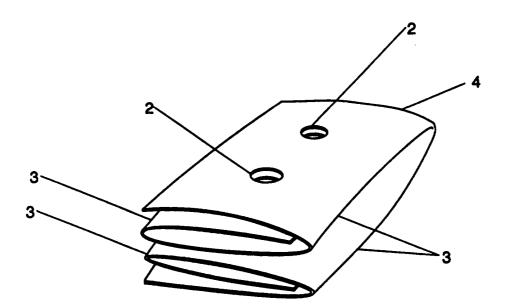
patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

#### **Published**

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: DRY CLEANING ARTICLE



### (57) Abstract

Articles especially adapted for in-home dry cleaning comprise a carrier sheet which is impregnated with a cleaning composition. The articles are designed to be folded for packaging, and to be unfolded during use. The articles are provided with holes which help maintain them in the unfolded configuration, especially during use in a hot-air clothes dryer.

### FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| AM | Armenia                  | GB | United Kingdom               | MW  | Malawi                   |
|----|--------------------------|----|------------------------------|-----|--------------------------|
| ΑT | Austria                  | GE | Georgia                      | MX  | Mexico                   |
| ΑU | Australia                | GN | Guinea                       | NE  | Niger                    |
| BB | Barbados                 | GR | Greece                       | NL  | Netherlands              |
| BE | Belgium                  | HU | Hungary                      | NO  | Norway                   |
| BF | Burkina Faso             | IE | Ireland                      | NZ  | New Zealand              |
| BG | Bulgaria                 | IT | Italy                        | PL  | Poland                   |
| BJ | Benin                    | JP | Japan                        | PT  | Portugal                 |
| BR | Brazil                   | KE | Kenya                        | RO  | Romania                  |
| BY | Belarus                  | KG | Kyrgystan                    | RU  | Russian Federation       |
| CA | Canada                   | KP | Democratic People's Republic | SD  | Sudan                    |
| CF | Central African Republic |    | of Korea                     | SE  | Sweden                   |
| CG | Congo                    | KR | Republic of Korea            | SG  | Singapore                |
| CH | Switzerland              | KZ | Kazakhstan                   | SI  | Slovenia                 |
| CI | Côte d'Ivoire            | LI | Liechtenstein                | SK  | Slovakia                 |
| CM | Cameroon                 | LK | Sri Lanka                    | SN  | Senegal                  |
| CN | China                    | LR | Liberia                      | SZ  | Swaziland                |
| CS | Czechoslovakia           | LT | Lithuania                    | TD  | Chad                     |
| CZ | Czech Republic           | LU | Luxembourg                   | TG  | Togo                     |
| DE | Germany                  | LV | Latvia                       | TJ  | Tajikistan               |
| DK | Denmark                  | MC | Monaco                       | TT  | Trinidad and Tobago      |
| EE | Estonia                  | MD | Republic of Moldova          | UA. | Ukraine                  |
| ES | Spain                    | MG | Madagascar                   | UG  | Uganda                   |
| FI | Finland                  | ML | Mali                         | US  | United States of America |
| FR | France                   | MN | Mongolia                     | UZ. | Uzbekistan               |
| GA | Gabon                    | MR | Mauritania                   | VN  | Viet Nam                 |

WO 96/30581 PCT/US96/02886

### DRY CLEANING ARTICLE

### FIELD OF THE INVENTION

The present invention relates to dry cleaning articles which are especially adapted for use in appliances such as laundry dryers.

# CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of co-pending Serial No. 08/413,332, filed March 30, 1995.

# 10 BACKGROUND OF THE INVENTION

5

15

20

25

30

35

By classical definition, the term "dry cleaning" has been used to describe processes for cleaning textiles using nonaqueous solvents. Dry cleaning is an old art, with solvent cleaning first being recorded in the United Kingdom in the 1860's. Typically, dry cleaning processes are used with garments such as woolens which are subject to shrinkage in aqueous laundering baths, or which are judged to be too valuable or too delicate to subject to aqueous laundering processes. Various hydrocarbon and halocarbon solvents have traditionally been used in immersion dry cleaning processes, and the need to handle and reclaim such solvents has mainly restricted the practice of conventional dry cleaning to commercial establishments.

While solvent-based dry cleaning processes are quite effective for removing oily soils and stains, they are not optimal for removing particulates such as clay soils, and may require special treatment conditions to remove proteinaceous stains. Ideally, particulates and proteinaceous stains are removed from fabrics using detersive ingredients and operating conditions which are more akin to aqueous laundering processes than to conventional dry cleaning.

In addition to the cleaning function, dry cleaning also provides important "refreshment" benefits. For example, dry cleaning removes undesirable odors and extraneous matter such as hair and lint from garments, which are then generally folded or pressed to remove wrinkles and restore their original shape. Of course, such refreshment benefits are also afforded by aqueous laundering processes.

As can be seen from the foregoing, and aside from the effects on certain fabrics such as woolens, there are no special, inherent advantages for solvent-based immersion dry cleaning over aqueous cleaning processes with respect to fabric cleaning or refreshment. Moreover, on a pergarment basis, commercial dry cleaning is much more expensive than aqueous cleaning processes.

While it would be of considerable benefit to consumers to provide non-immersion dry cleaning compositions and processes which can be used in the home, the typical solvent systems used in commercial dry cleaning render this impractical. Indeed, various in-home dry cleaning systems have been suggested, but have not been widely accepted.

45

50

55

60

65

70

In one type of home dry cleaning system, a carrier sheet comprising various cleaning agents and a bag are provided. In a commercial embodiment, multiple single-use sheets and a single multiuse plastic bag are provided in a single package. Since the sheets are relatively large, they are folded for ease-of-packaging. In use, a sheet is unfolded, placed in the reusable bag together with the fabrics to be cleaned, and tumbled in a conventional hot air clothes dryer. Of course, in order to function optimally, the surfaces of the fabrics must come in contact with the surface or surfaces of the carrier sheet containing the cleaning compositions. Such contact is most efficiently achieved only when the sheet remains in a substantially open, unfolded configuration. Unfortunately, it has now been discovered that such sheets have a tendency to partially or completely re-close by refolding along their original fold lines or creases, thereby resulting in sub-optimal contact with the fabrics and, hence, sub-optimal cleaning performance.

By the present invention, it has been discovered that the tendency of the above-described sheets to re-fold and re-close along their original fold lines can be substantially diminished or prevented by perforating the sheets in the manner disclosed herein. This results in improved cleaning performance. Accordingly, it is an object of the present invention to provide improved sheets for use in a dry cleaning operation. Another object is to provide improved cleaning performance in a home dry cleaning process. Yet another object is to provide dry cleaning sheets which can be folded for packaging without loss of their in-use cleaning performance. These and other objects are secured herein, as will be seen from the following disclosure.

#### **BACKGROUND ART**

Dry cleaning processes are disclosed in: EP 429,172A1, published 29.05.91, Leigh, et al.; and in U.S. 5,238,587, issued 8/24/93, Smith, et al. Other references relating to dry cleaning compositions and processes, as well as wrinkle treatments for fabrics, include: GB 1,598,911; and U.S. Patents 4,126,563, 3,949,137, 3,593,544, 3,647,354; 3,432,253 and 1,747,324; and German applications 2.021,561 and 2,460,239, 0,208,989 and 4,007,362. Cleaning/pre-spotting compositions and methods are also disclosed, for example, in U.S. Patents 5,102,573; 5,041,230; 4,909,962; 4,115,061; 4,886,615; 4,139,475; 4,849,257; 5,112,358; 4,659,496; 4,806,254; 5,213,624; 4,130,392; and 4,395,261. Sheet substrates for use in a laundry dryer are disclosed in Canadian 1,005,204. U.S. 3,956,556 and 4,007,300 relate to perforated sheets for fabric conditioning in a clothes dryer. U.S. 4,692,277 discloses the use of 1,2-octanediol in liquid cleaners.

### **SUMMARY OF THE INVENTION**

The present invention encompasses a fabric cleaning article comprising a flexible sheet substrate carrying a cleaning composition removable to fabrics by contact therewith, said sheet substrate having fold lines, said sheet substrate also having perforations sufficient in size and number to substantially diminish or prevent the tendency of said sheet substrate when in an open configuration, in-use, to close by re-folding along said fold lines. In one mode, the perforations comprise a plurality of circular holes; however, other shapes such as triangles, squares and other

80

90

100

105

110

polyhedra are equivalent and may be used. Slitted sheets are also useful, but are not as preferred as those with holes. In a typical mode, the holes have a diameter of from about 0.3 cm to about 2.0 cm.

In order to provide optimal results, the perforations will comprise from about 0.7% to about 15% of the area of the sheet substrate. Thus, in a preferred article herein, the area of the sheet substrate is from about  $360 \text{ cm}^2$  to about  $3000 \text{ cm}^2$ , and the perforations will comprise from about 0.7% to about 15%, more preferably from about 0.7% to about 8.0%, of the area of the sheet substrate.

The invention also encompasses a method for cleaning fabrics in a tumbling apparatus, comprising placing said fabrics in a container together with a perforated article as described above which is in an unfolded configuration, closing said container, and tumbling said fabrics together with said unfolded article. The method is conveniently conducted in a hot air clothes dryer.

The invention also encompasses a dry cleaning composition in kit form, comprising the following components:

- (a) multiple, folded fabric cleaning articles as disclosed herein which, typically, are intended for a single usage;
- (b) a reusable container, especially a plastic bag, for use in a hot air clothes dryer or other, equivalent, tumbling apparatus; and
  - (c) an outer package containing said components (a) and (b).

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

# BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a perspective of the sheet of the present invention in a folded configuration.

Figure 2 is a plan view of the sheet of the present invention in an unfolded configuration.

### DETAILED DESCRIPTION OF THE INVENTION

The carrier sheets for the cleaning compositions herein and their use in the dry cleaning process of the present invention are described hereinafter.

<u>Carrier Sheet Substrate</u> - The carrier herein is in the form of an integral sheet which substantially maintains its structural integrity throughout the cleaning process. Such sheets can be prepared, for example, using well-known methods for manufacturing non-woven sheets, paper towels, fibrous batts, cores for bandages, diapers and catamenials, and the like, using materials such as wood pulp, cotton, rayon, polyester fibers, and mixtures thereof. Woven cloth sheets may also be used, but are not preferred over non-woven sheets due to cost considerations. Integral carrier sheets or sheets may also be prepared from natural or synthetic sponges, foams, and the like.

The carrier sheets are designed to be safe and effective under the intended operating conditions of the present process. The carrier sheets must not be flammable during the process, nor should they deleteriously interact with the cleaning composition or with the fabrics being cleaned. In general, non-woven polyester-based sheets are quite suitable for use as the carrier herein.

120

125

130

135

140

145

The carrier sheets used herein are most preferably lint-resistant. By "lint-resistant" herein is meant a sheet which resists the shedding of visible fibers or microfibers onto the fabrics being cleaned, i.e., the deposition of what is known in common parlance as "lint". A carrier sheet can easily and adequately be judged for its acceptability with respect to lint resistance by rubbing it on a piece of dark blue woolen cloth and visually inspecting the cloth for lint residues.

The lint-resistance of the carrier sheets used herein can be achieved by several means, including but not limited to: preparing the carrier sheet from a single strand of fiber; and employing known bonding techniques commonly with nonwoven materials, e.g., point bonding, print bonding, adhesive/resin saturation bonding, adhesive/resin spray bonding, stitch bonding and bonding with binder fibers. In an alternate mode, a carrier can be prepared using an absorbent core, said core being made from a material which, itself, is not lint-resistant. The core is then enveloped within a sheet of porous, lint-resistant material having a pore size which allows passage of the cleaning compositions herein but through which lint from the core cannot pass. An example of such a carrier comprises a cellulose fiber core enveloped in a non-woven polyester scrim.

The carrier sheets should be of a size which provides sufficient surface area that effective contact between the surface of the carrier and the surface of the fabrics being cleaned is achieved. Of course, the size of the sheets should not be so large as to be unhandy for the user. Typically, the dimensions of a sheet will be sufficient to provide a macroscopic total surface area (both sides of the sheet) of at least about 360 cm<sup>2</sup>, preferably in the range from about 360 cm<sup>2</sup> to about 3000 cm<sup>2</sup>. For example, a rectangular sheet may have the dimensions (x-direction) of from about 20 cm to about 35 cm, and (y-direction) of from about 18 cm to about 45 cm.

The carrier sheet is intended to contain a sufficient amount of the cleaning composition to be effective for its intended purpose. The capacity of the carrier for the cleaning composition will vary according to the intended usage. For example, carrier/cleaning composition sheets which are intended for a single use will require less capacity than such sheets which are intended for multiple uses. For a given type of carrier the capacity for the cleaning composition will vary mainly with the thickness or "caliper" (z-direction; dry basis) of the sheet. For purposes of illustration, typical single-use polyester sheets used herein will have a thickness in the range from about 0.1 mm to about 0.7 mm and a basis weight in the range from about 30 g/m<sup>2</sup> to about 100 g/m<sup>2</sup>. Typical multi-use polyester sheets herein will have a thickness in the range from about 0.2 mm to about 1.0 mm and a basis weight in the range from about 40 g/m<sup>2</sup> to about 150 g/m<sup>2</sup>. Open-cell sponge sheets will range in thickness from about 0.1 mm to about 1.0 mm. Of course, the foregoing dimensions may vary, as long as the desired quantity of the cleaning composition is effectively provided by means of the carrier.

With reference to Figure 2, the carrier sheet (1) is provided with a plurality of holes (2) which cause it to remain open along vertical fold lines (3) and horizontal fold line (4), in-use in the dry cleaning operation.

155

160

165

170

175

180

The holes can be punched through the sheet in any convenient manner. If the sheet has too many holes, it may be inconvenient to use for pre-spotting in the manner described hereinafter. If the holes are too few, or too small, the article tends not to remain in the desired open configuration during use. A convenient and effective hole size is about 1.27 cm in diameter. For a 25 cm x 25 cm sheet, about 12 such holes are quite effective for maintaining the sheet in an open configuration in use in a hot air clothes dryer.

Cleaning Compositions - The chemical compositions which are used to provide the cleaning function in the present dry cleaning process comprise ingredients which are safe and effective for their intended use. Since the process herein does not involve an aqueous rinse step, the cleaning compositions employ ingredients which do not leave undesirable residues on fabrics when employed in the manner disclosed herein. Moreover, since the process may be carried out in a hot air clothes dryer, the compositions contain only ingredients whose flash points render them safe for such use. The cleaning compositions contain water, since water not only aids in the cleaning function, but also can help remove wrinkles and restore fabric drape and appearance, especially in hot air dryers. While conventional laundry detergents are typically formulated to provide good cleaning on cotton and cotton/polyester blend fabrics, the cleaning compositions herein must be formulated to also safely and effectively clean and refresh fabrics such as wool, silk, rayon, rayon acetate, and the like.

In addition, the cleaning compositions herein comprise ingredients which are specially selected and formulated to minimize dye removal from the fabrics being cleaned. In this regard, it is recognized that the solvents typically used in immersion dry cleaning processes can remove some portion of certain types of dyes from certain types of fabrics. However, such removal is tolerable in immersion processes since the dye is removed relatively uniformly across the surface of the fabric. In contrast, it has now been determined that high concentrations of certain types of cleaning ingredients at specific sites on fabric surfaces can result in unacceptable localized dye removal. The preferred cleaning compositions herein are formulated to minimize or avoid this problem.

The dye removal attributes of the present cleaning compositions can be compared with art-disclosed cleaners using photographic or photometric measurements, or by means of a simple, but effective, visual grading test. Numerical score units can be assigned to assist in visual grading and to allow for statistical treatment of the data, if desired. Thus, in one such test, a colored garment (typically, silk, which tends to be more susceptible to dye loss than most woolen or rayon fabrics) is treated by padding-on cleaner using an absorbent, white paper hand towel. Hand pressure is applied, and the amount of dye which is transferred onto the white towel is assessed visually. Numerical units ranging from: (1) "I think I see a little dye on the towel"; (2) "I know I see some dye on the towel"; (3) I see a lot of dye on the towel"; through (4) "I know I see quite a lot of dye on the towel" are assigned by panelists.

In addition to the foregoing considerations, the cleaning composition herein is preferably formulated such that it is not so adhesive in nature that it renders the articles unhandy or difficult to unfold from their package, and they should remain in the unfolded configuration during use. Moreover, while it is acceptable that the articles herein be moist to the touch, they preferably do not have a slimy or adhesive feel. The acceptability of the articles in regard to such matters can be judged without undue experimentation. However, and while not intending to be limiting of the present invention, the following cleaning compositions afford articles of the present type which are both effective for their intended cleaning and fabric refreshment purposes and aesthetically pleasing.

Having due regard to the foregoing considerations, the following illustrates the ingredients used in the cleaning compositions herein, but is not intended to be limiting thereof.

- (a) Water -The compositions will comprise at least about 60%, typically from about 80% to about 95%, by weight, of water. Stated otherwise, the objective is to provide at least about 6 g of water per kg of fabrics being cleaned.
- (b) Solvent The compositions will comprise at least about 4%, typically from about 5% to about 25%, by weight, of organic solvent. The objective is to provide at least about 0.4 g, preferably from about 0.5 g to about 2.5 g, of solvent per kg of fabrics being cleaned.
- (c) Emulsifier The compositions will comprise sufficient emulsifier to provide a stable, homogeneous composition comprising components (a), (b) and (d). For the preferred emulsifiers disclosed hereinafter, levels as low as 0.05%, preferably 0.07% to about 0.20%, by weight, are quite satisfactory. If less efficient emulsifiers are used, levels up to about 2%, by weight, can be used, but may leave some noticeable residues on the fabrics.
- (d) Optionals The compositions herein may comprise various optional ingredients, including perfumes, conventional surfactants, and the like. If used, such optional ingredients will typically comprise from about 0.1% to about 10%, by weight, of the compositions, having due regard for residues on the cleaned fabrics.

It has now been determined that 1,2-octanediol ("OD") affords special advantages in the formulation of the cleaning compositions herein. From the standpoint of aesthetics, OD is a relatively innocuous and low odor material. Moreover, OD appears to volatilize from fabric surfaces without leaving visible residues. This is especially important in a dry cleaning process of the present type which is conducted without a rinse step. From the performance standpoint, OD appears to function both as a solvent for greasy/oily stains and as what might be termed a "pseudo-surfactant" for particulate soils and water-soluble stains. Whatever the physical-chemical reason, OD has now been found to be a superior wetting agent with respect to both cleaning and ease-of-use in the present context of home-use cleaning compositions and processes.

195

190

200

205

210

215

230

235

240

245

A preferred solvent herein is butoxy propoxy propanol (BPP) which is available in commercial quantities as a mixture of isomers in about equal amounts. The isomers, and mixtures thereof, are useful herein. The isomer structures are as follows:

BPP is outstanding for cleaning, and is so effective that it allows the amount of the relatively expensive 1,2-octanediol to be minimized. Moreover, it allows for the formulation of effective cleaning compositions herein without the use of conventional surfactants. Importantly, the odor of BPP is of a degree and character that it can be relatively easily masked by conventional perfume ingredients. While BPP is not completely miscible with water and, hence, could negatively impact processing of the cleaning compositions herein, that potential problem has been successfully overcome by means of the PEMULEN-type polyacrylate emulsifiers, as disclosed hereinafter.

The BPP solvent used herein is preferably a mixture of the aforesaid isomers. In a preferred mode, the cleaning compositions comprise a mixture of the 1,2-octanediol and BPP, at a weight ratio of OD:BPP in the range of from about 1:250 to about 2:1, preferably from about 1:200 to about 1:5.

A highly preferred emulsifier herein is commercially available under the trademark PEMULEN, The B. F. Goodrich Company, and is described in U.S. Patents 4,758,641 and 5,004,557, incorporated herein by reference. PEMULEN polymeric emulsifiers are high molecular weight polyacrylic acid polymers. The structure of PEMULEN includes a small portion that is oilloving (lipophilic) and a large water-loving (hydrophilic) portion. The structure allows PEMULEN to function as a primary oil-in-water emulsifier. The lipophilic portion adsorbs at the oil-water interface, and the hydrophilic portion swells in the water forming a network around the oil droplets to provide emulsion stability. An important advantage for the use of such polyacrylate emulsifiers herein is that cleaning compositions can be prepared which contain solvents or levels of solvents that are otherwise not soluble or readily miscible with water. A further advantage is that effective emulsification can be accomplished using PEMULEN-type emulsifier at extremely low usage levels (0.05-0.2%), thereby minimizing the level of any residue left on fabrics following product usage. For comparison, typically about 3-7% of conventional anionic or nonionic surfactants are required to stabilize oil-in-water emulsions, which increases the likelihood that a residue will be left on the fabrics. Another advantage is that emulsification (processing) can be accomplished effectively at room temperature.

265

270

275

280

285

While the cleaning compositions herein function quite well with only the 1.2-octanediol, BPP, PEMULEN and water, they may also optionally contain detersive surfactants to further enhance their cleaning performance. While a wide variety of detersive surfactants such as the C<sub>12</sub>-C<sub>16</sub> alkyl sulfates and alkylbenzene sulfonates, the C<sub>12</sub>-C<sub>16</sub> ethoxylated (EO 0.5-10 avg.) alcohols, the C<sub>12</sub>-C<sub>14</sub> N-methyl glucamides, and the like can be used herein, it is highly preferred to use surfactants which provide high grease/oil removal. Included among such preferred surfactants are the C<sub>12</sub>-C<sub>16</sub> alkyl ethoxy sulfates (AES), especially in their magnesium salt form, and the C<sub>12</sub>-C<sub>16</sub> dimethyl amine oxides. An especially preferred mixture comprises MgAE<sub>1</sub>S/MgAE<sub>6.5</sub>S/C<sub>12</sub> dimethyl amine oxide, at a weight ratio of about 1:1:1. If used, such surfactants will typically comprise from about 0.05% to about 2.5%, by weight, of the cleaning compositions herein.

In addition to the preferred solvents and emulsifiers disclosed above, the cleaning compositions herein may comprise various optional ingredients, such as perfumes, preservatives, cosolvents, brighteners, salts for viscosity control, pH adjusters or buffers, anti-static agents, softeners, colorants, mothproofing agents, insect repellents, and the like.

<u>Container</u> - The present cleaning process is conducted using a flexible container. The fabrics to be cleaned are placed within the container with the carrier/cleaning composition article, and the container is agitated, thereby providing contact between the carrier/cleaning composition and the surfaces of the fabrics.

The flexible container used herein can be provided in any number of configurations, and is conveniently in the form of a flexible pouch, or "bag", which has sufficient volume to contain the fabrics being cleaned. The container can be of any convenient size, and should be sufficiently large to allow tumbling of the container and fabrics therein, but should not be so large as to interfere with the operation of the tumbling apparatus. With special regard to containers intended for use in hot air clothes dryers, the container must not be so large as to block the air vents. If desired, the container may be small enough to handle only a single shirt, blouse or sweater, or be sufficiently large to handle a man's suit. Suitable containers can be manufactured from any economical material, such as polyester, polypropylene, and the like, with the priviso that it must not melt if used in contact with hot dryer air. It is preferred that the walls of the container be substantially impermeable to water vapor and solvent vapor under the intended usage conditions. It is also preferred that such containers be provided with a sealing means which is sufficiently stable to remain closed during the cleaning process. Simple tie strings or wires, various snap closures such as ZIP LOK® closures, and VELCRO®-type closures, contact adhesives, adhesive tape, zipper-type closures, and the like, suffice.

<u>Process</u> - The present cleaning process can be conducted in any manner which provides mechanical agitation, such as a tumbling action, to the container with the fabrics being cleaned. If desired, the agitation may be provided manually. However, in a convenient mode a container with the carrier/cleaning composition and enveloping the soiled fabric is sealed and placed in the drum of

295

315

320

an automatic clothes dryer. The drum is allowed to revolve, which imparts a tumbling action to the container and agitation of its contents concurrently with the tumbling. By virtue of this agitation, the fabrics come in contact with the carrier releasably containing the cleaning composition. It is preferred that heat be employed during the process. Of course, heat can easily be provided in a clothes dryer. The tumbling and optional (but preferred) heating is carried out for a period of at least about 10 minutes, typically from about 20 minutes to about 30 minutes. The process can be conducted for longer or shorter periods, depending on such factors as the degree and type of soiling of the fabrics, the nature of the soils, the nature of the fabrics, the fabric load, the amount of heat applied, and the like, according to the needs of the user.

The following illustrates a typical article in more detail, but is not intended to be limiting thereof.

#### EXAMPLE I

A dry cleaning article in sheet form is assembled using a sheet substrate and a cleaning composition prepared by admixing the following ingredients.

|     | Ingredient     | <u>% (wt.)</u> |
|-----|----------------|----------------|
|     | BPP*           | 7.0            |
|     | 1,2-octanediol | 0.5            |
|     | PEMULEN TR-1** | 0.15           |
| 305 | КОН            | 0.08           |
|     | Perfume        | 0.75           |
|     | Water          | Balance        |

<sup>\*</sup>Isomer mixture, available from Dow Chemical Co.

The cleaning composition can also optionally contain 0.50% (wt.) of a mixture of MgAE<sub>1</sub>S. MgAE<sub>6.5</sub>S and C<sub>12</sub> amine oxide surfactants, in the range of 1:1:1 to 0.5:1:1.

A non-linting carrier sheet is prepared using a non-woven two-ply fabric stock comprising polyester fibers, caliper 0.25 mm to 0.34 mm, basis weight 84 g/m $^2$ . The fabric is cut into square carrier sheets, approximately 25 cm on a side, i.e., 625 cm $^2$  sheets. Three or four rows of regularly-spaced 1.27 cm (0.5 inch) diameter circular holes are punched through the sheet as shown in Figure 2.

23 Grams of the above-noted cleaning composition are evenly applied to the sheet by spreading onto the sheet with a roller or spatula using hand pressure. In an alternative mode, the cleaning composition can be applied by dipping or spraying the composition onto the substrate, followed by squeezing with a roller or pair of nip rollers, i.e., by "dip-squeezing" or "spray squeezing". The external surfaces of the sheet are damp but not tacky to the touch.

<sup>\*\*</sup>PEMULEN TR-2, B. F. Goodrich, may be substituted.

Dry cleaning sheets prepared in the foregoing manner are ready for use in the manner disclosed in Example II, or for folding such as shown in Figure 1 and packaging in kit form in the manner disclosed in Example III, hereinafter.

325

330

335

340

### **EXAMPLE II**

The following illustrates a typical process herein in more detail, but is not intended to be limiting thereof.

A dry cleaning sheet of the type described in Example I is unfolded along the fold lines (3) and (4) as shown in Figure 2 and placed in a plastic bag having a volume of about 25,000 cm<sup>3</sup> together with up to about 2 kg of dry garments to be cleaned. When the garments and the dry cleaning sheet are placed in the bag, the air is preferably not squeezed out of the bag before closing and sealing. This allows the bag to billow, thereby providing sufficient space for the tabrics and cleaning sheet to tumble freely together. The bag is then closed, sealed and placed in a conventional hot-air clothes dryer. The dryer is started and the bag is tumbled for a period of 20-30 minutes at a dryer air temperature in the range from about 50°C to about 85°C. During this time, the dry cleaning sheet remains substantially in the desired open position, thereby providing effective contact with the fabrics. After the machine cycle is complete, the bag and its contents are removed from the dryer, and the spent dry cleaning sheet is discarded. The plastic bag is retained for re-use. The fabrics are cleaned and refreshed. The water present in the cleaning composition serves to minimize wrinkles in the fabrics.

In an alternate mode, heavily soiled areas of the fabric being cleaned can optionally be pretreated by pressing or rubbing a fresh dry cleaning sheet according to this invention on the area. The sheet and pre-treated fabric are then placed in the container, and the dry cleaning process is conducted in the manner described herein.

345

350

### **EXAMPLE III**

The following illustrates a typical dry cleaning kit herein, but is not intended to be limiting thereof.

A dry cleaning kit is assembled by folding and packaging multiple (typically, five) single use dry cleaning sheets of the type described herein and depicted in the Figures, together with a sealable, reusable plastic container bag, in a package comprising a conventional cardboard box suitable for retail sales.

Having thus described and exemplified the present invention, the following further illustrates various cleaning compositions which can be formulated and used in the practice thereof.

### **EXAMPLE IV**

| 355 | Ingredient          | % (wt.) Formula Range |
|-----|---------------------|-----------------------|
|     | BPP*                | 5-25%                 |
|     | 1.2-Octanediol      | 0.1-7%                |
|     | MgAE <sub>1</sub> S | 0.01-0.8%             |

|     | MgAE <sub>6.5</sub> S                | 0.01-0.8%  |
|-----|--------------------------------------|------------|
| 360 | C <sub>12</sub> Dimethyl Amine Oxide | 0.01-0.8%  |
|     | PEMULEN**                            | 0.05-0.20% |
|     | Perfume                              | 0.01-1.5%  |
|     | Water                                | Balance    |
|     |                                      |            |

pH range from about 6 to about 8.

\*Other solvents or co-solvents which can be used herein include various glycol ethers, including materials marketed under trademarks such as Carbitol, methyl Carbitol, butyl Carbitol, propyl Carbitol, and hexyl Cellosolve, and especially methoxy propoxy propanol (MPP), ethoxy propoxy propanol (EPP), propoxy propoxy propanol (PPP), and all isomers and mixtures, respectively, of MPP, EPP, and PPP, and the like, and mixtures thereof. Indeed, although somewhat less preferred, the MPP, EPP and PPP, respectively, can replace the BPP solvent in the foregoing cleaning compositions. The levels of these solvents, and their ratios with 1.2-octanediol, are the same as with the preferred BPP solvent. If desired, and having due regard for safety and odor for in-home use, various conventional chlorinated and hydrocarbon dry cleaning solvents may also be used. Included among these are 1,2-dichloroethane, trichloroethylene, isoparaffins, and mixtures thereof.

\*\*As disclosed in U.S. Patents 4,758,641 and 5,004,557, such polyacrylates include homopolymers which may be crosslinked to varying degrees, as well as non-crosslinked. Preferred herein are homopolymers having a molecular weight in the range of from about 100,000 to about 10,000,000, preferably 200,000 to 5,000,000.

Excellent cleaning performance is secured using any of the foregoing non-immersion processes and articles to provide from about 5 g to about 50 g of the cleaning compositions per kilogram of fabric being cleaned.

### **EXAMPLE V**

A dry cleaning composition with reduced tendency to cause dye "bleeding" or removal from fabrics as disclosed above is as follows.

| 385 | INGREDIENT                     | PERCENT (wt.) | (RANGE) |              |
|-----|--------------------------------|---------------|---------|--------------|
|     | Butoxypropoxy propanol (BPP)   | 7.000         |         | 4.0 - 25.0%  |
|     | NEODOL 23 - 6.5*               | 0.750         |         | 0.05 - 2.5%  |
|     | 1.2-Octanediol                 | 0.500         |         | 0.1 - 10.0%  |
|     | Perfume                        | 0.750         |         | 0.1 - 2.0%   |
| 390 | Pemulen TR-1                   | 0.125         |         | 0.05 - 0.2%  |
|     | Potassium Hydroxide (KOH)      | 0.060         |         | 0.024 - 0.10 |
|     | Potassium Chloride             | 0.075         |         | 0.02 - 0.20  |
|     | Water (distilled or deionized) | 90.740        |         | 60.0 - 95.0% |
|     | Target $pH = 7.0$              |               |         |              |
| 205 |                                |               |         |              |

\*Shell; C<sub>12</sub>-C<sub>13</sub> alcohol, ethoxylated with average EO of 6.5.

405

410

415

420

425

430

15-25 Grams of a composition of the foregoing type are placed on a carrier sheet for use in the manner disclosed herein. A preferred carrier substrate comprises a binderless (or optional low binder), hydroentangled absorbent material, especially a material which is formulated from a blend of cellulosic, rayon, polyester and optional bicomponent fibers. Such materials are available from Dexter, Non-Wovens Division, The Dexter Corporation as HYDRASPUN®, especially Grade 10244. The manufacture of such materials forms no part of this invention and is already disclosed in the literature. See, for example, U.S. Patents 5,009,747, Viazmensky, et al., April 23, 1991 and 5,292,581, Viazmensky, et al., March 8, 1994, incorporated herein by reference.

Surprisingly, this hydroentangled carrier is not merely a passive absorbent for the cleaning compositions herein, but actually optimizes cleaning performance. While not intending to be limited by theory, it may be speculated that this carrier is more effective in delivering the cleaning composition to soiled fabrics. Or, this particular carrier might be better for removing soils by contact with the soiled fabrics, due to its mixture of fibers. Whatever the reason, improved dry cleaning performance is secured.

A perforated sheet of the foregoing type is placed together with the fabrics to be dry cleaned in a flexible containment bag having dimensions as noted hereinabove and sealing means. In a preferred mode, the containment bag is constructed of thermal resistant film in order to provide resistance to hot spots (350°F-400°F; 177°C to 204°C) which can develop in some dryers. This avoids internal self-sealing and external surface deformation of the bag, thereby allowing the bag to be re-used.

In a preferred embodiment, 0.0025 mm to 0.0075 mm thickness nylon film is converted into a 26 inch (66 cm) x 30 in. (76 cm) bag. Bag manufacture can be accomplished in a conventional manner using standard impulse heating equipment, air blowing techniques, and the like. In an alternate mode, a sheet of nylon is simply folded in half and sealed along two of its edges.

In addition to thermally stable "nylon-only" bags, the containment bags herein can also be prepared using sheets of co-extruded nylon and/or polyester or nylon and/or polyester outer and/or inner layers surrounding a less thermally suitable inner core such as polypropylene. In an alternate mode, a bag is constructed using a nonwoven outer "shell" comprising a heat-resistant material such as nylon or polyethylene terephthalate and an inner sheet of a polymer which provides a vapor barrier. The non-woven outer shell protects the bag from melting and provides an improved tactile impression to the user. Whatever the construction, the objective is to protect the bag's integrity under conditions of thermal stress at temperatures up to at least about 400-500°F (204°C to 260°C). Nylon VELCRO®-type, ZIP-LOK®-type and/or zipper-type closures can be used to seal the bag, in-use.

Besides the optional nonionic surfactants used in the cleaning compositions herein, which are preferably C<sub>8</sub>-C<sub>18</sub> ethoxylated (E01-15) alcohols or the corresponding ethoxylated alkyl

450

phenols, the compositions used herein can contain enzymes to further enhance cleaning performance. Lipases, amylases and protease enzymes, or mixtures thereof, can be used. If used, such enzymes will typically comprise from about 0.001% to about 5%, preferably from about 0.01% to about 1%, by weight, of the composition. Commercial detersive enzymes such as LIPOLASE, ESPERASE, ALCALASE, SAVINASE and TERMAMYL (all ex. NOVO) and MAXATASE and RAPIDASE (ex. International Bio-Synthesis, Inc.) can be used.

If an antistatic benefit is desired, the compositions used herein can contain an anti-static agent. If used, such anti-static agents will typically comprise at least about 0.5%, typically from about 2% to about 8%, by weight, of the compositions. Preferred anti-stats include the series of sulfonated polymers available as VERSAFLEX 157, 207, 1001, 2004 and 7000, from National Starch and Chemical Company.

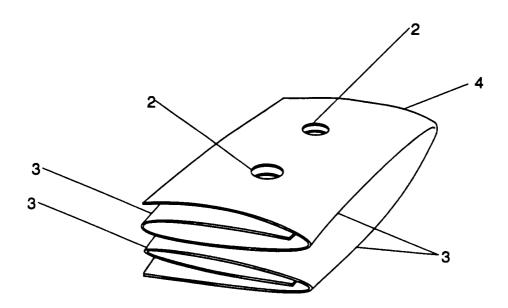
The compositions herein can optionally be stabilized for storage using conventional preservatives such as KATHON® at a level of 0.001%-1%, by weight.

If the compositions herein are used in a spot-cleaning mode, they are preferably pressed (not rubbed) onto the fabric at the spotted area using an applicator pad comprising looped fibers, such as is available as APLIX 200 or 960 Uncut Loop, from Aplix, Inc., Charlotte, NC. An underlying absorbent sheet or pad of looped fibers can optionally be placed beneath the fabric in this mode of operation.

#### WHAT IS CLAIMED IS:

- 1. A fabric cleaning article comprising a flexible sheet substrate carrying a cleaning composition removable to fabrics by contact therewith, characterized by said sheet substrate having fold lines, and wherein said sheet substrate has perforations sufficient in size and number to substantially diminish or prevent the tendency of said sheet substrate when in-use in an open configuration to close by re-folding along said fold lines.
- 2. An article according to Claim 1 wherein the perforations comprise a plurality of holes.
  - 3. An article according to Claim 2 wherein the holes have a diameter of from 0.3 cm to about 2.0 cm.
- 4. An article according to Claim 1 wherein the perforations comprise from 0.7% to 15% of the area of the sheet substrate.
- 5. An article according to Claim 4 wherein the surface area of the sheet substrate is from 360 cm<sup>2</sup> to 3000 cm<sup>2</sup>, and wherein the perforations comprise from 0.7% to 8.0% of the area of the sheet substrate.
  - 6. A method for cleaning fabrics in a tumbling apparatus, comprising placing said fabrics in a container together with an article according to Claim 1, characterized in that said article is in an unfolded configuration, closing said container, and tumbling said fabrics together with said unfolded article.
    - A method according to Claim 6 which is conducted in a hot air clothes dryer.
    - 8. A dry cleaning composition in kit form, characterized in that it comprises:
- 30 (a) multiple, folded fabric cleaning articles according to Claim 1;
  - (b) a reusable container suitable for use in a hot air clothes dryer; and
  - (c) an outer package containing said components (a) and (b).

25



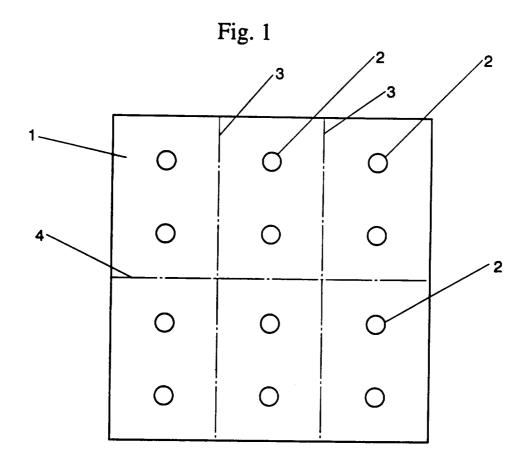


Fig. 2

# INTERNATIONAL SEARCH REPORT

Inter nal Application No PCT/US 96/02886

| IPC 6         | SIFICATION OF SUBJECT MATTER D06F43/00                                                                              |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                        |
|---------------|---------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------|
| According     | to International Patent Classification (IPC) or to both national classification                                     | ssification and IPC                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                        |
|               | S SEARCHED                                                                                                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                        |
| IPC 6         | documentation searched (classification system followed by classific $D06F$                                          | ation symbols)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                        |
| Documenta     | ation searched other than minimum documentation to the extent tha                                                   | at such documents are included in the fields                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | searched               |
|               |                                                                                                                     | and the state of t | real circu             |
|               |                                                                                                                     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                        |
| Electronic    | data base consulted during the international search (name of data b                                                 | ase and, where practical, search terms used)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                        |
| C. DOCUN      | MENTS CONSIDERED TO BE RELEVANT                                                                                     |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                        |
| Category *    | Citation of document, with indication, where appropriate, of the                                                    | relevant passages                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | Relevant to claim No.  |
| А             | EP,A,0 429 172 (UNILEVER PLC) 29 cited in the application see claims                                                | May 1991                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 1,6,7                  |
| A             | US,A,5 238 587 (CREATIVE PRODUCT<br>ASSOCIATES) 24 August 1993<br>cited in the application<br>see claim 19          | 'S RESOURCE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | 1,6,7                  |
| Α             | US,A,4 012 540 (THE PROCTER & GA<br>COMPANY) 15 March 1977<br>see claims; figures                                   | MBLE                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 1-5                    |
| A             | GB,A,1 598 911 (KENNETH DAVID GO<br>September 1981<br>cited in the application<br>see the whole document            | MM) 23                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | 1,6-8                  |
| Furth         | ner documents are listed in the continuation of box C.                                                              | X Patent family members are listed in                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | in annex.              |
| * Special cat | egories of cited documents :                                                                                        | "T" later document published after the inte                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | emetional filips date  |
| 'A' docume    | ent defining the general state of the art which is not<br>ared to be of particular relevance                        | or priority date and not in conflict wi<br>cited to understand the principle or th                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             | th the application but |
| E' earlier o  | document but published on or after the international                                                                | invention "X" document of particular relevance; the                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | , , ,                  |
| filing d      | nt which may throw doubts on priority claim(s) or                                                                   | cannot be considered novel or cannot involve an inventive step when the do                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     | be considered to       |
| citation      | s cited to establish the publication date of another or other special reason (as specified)                         | "Y" document of particular relevance; the cannot be considered to involve an in-                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               | ventive step when the  |
| other m       |                                                                                                                     | document is combined with one or me<br>ments, such combination being obvious<br>in the art.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                        |
| later th      | nt published prior to the international filing date but<br>an the priority date claimed                             | '&' document member of the same patent                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | family                 |
| Date of the a | actual completion of the international search                                                                       | Date of mailing of the international ser                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | arch report            |
| 5             | July 1996                                                                                                           | 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 19.07.96               |
| Name and m    | ailing address of the ISA                                                                                           | Authorized officer                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                        |
|               | European Patent Office, P.B. 5818 Patentiaan 2<br>NL - 2280 HV Rijswijk<br>Tel (+ 31.70) 340.2040 Tv. 31.651 and al |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |                        |
|               | Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016                                                | Courrier, G                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |                        |

# INTERNATIONAL SEARCH REPORT

information on patent family members

Intern al Application No PCT/US 96/02886

| Patent document cited in search report | Publication date | Patent family member(s)                                      |                                                                          | Publication<br>date                                                              |
|----------------------------------------|------------------|--------------------------------------------------------------|--------------------------------------------------------------------------|----------------------------------------------------------------------------------|
| EP-A-429172                            | 29-05-91         | AU-B-<br>AU-B-<br>CA-A-<br>JP-A-                             | 629055<br>6459490<br>2027148<br>3130473                                  | 24-09-92<br>18-04-91<br>17-04-91<br>04-06-91                                     |
| US-A-5238587                           | 24-08-93         | CA-A-<br>EP-A-<br>JP-T-<br>WO-A-                             | 2135746<br>0640156<br>7509629<br>9323603                                 | 25-11-93<br>01-03-95<br>26-10-95<br>25-11-93                                     |
| US-A-4012540                           | 15-03-77         | US-A-<br>BE-A-<br>CA-A-<br>DE-A-<br>FR-A,B<br>GB-A-<br>NL-A- | 3944694<br>813204<br>1033917<br>2415247<br>2224583<br>1427305<br>7404454 | 16-03-76<br>02-10-74<br>04-07-78<br>24-10-74<br>31-10-74<br>10-03-76<br>07-10-74 |
| GB-A-1598911                           | 23-09-81         | NONE                                                         |                                                                          |                                                                                  |