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<p>(21) International Application Number: PCT/US99/30411</p> <p>(22) International Filing Date: 21 December 1999 (21.12.99)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>60/113,687</td> <td>24 December 1998 (24.12.98)</td> <td>US</td> </tr> <tr> <td>09/468,399</td> <td>20 December 1999 (20.12.99)</td> <td>US</td> </tr> </table> <p>(71) Applicant: ALLIEDSIGNAL, INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).</p> <p>(72) Inventors: WILSON, David, Paul; 118 Waxwing Court, East Amherst, NY 14051 (US). SINGH, Rajiv, Ratna; 18 Foxfire Drive, Getzville, NY 14068 (US). SHANKLAND, Ian, Robert; 6 Horizon Court, Randolph, NJ 07869 (US).</p> <p>(74) Agents: CRISS, Roger, H. et al.; AlliedSignal Inc. (Law Dept., Attn: A. Olinger), 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).</p>	60/113,687	24 December 1998 (24.12.98)	US	09/468,399	20 December 1999 (20.12.99)	US	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published</p> <p><i>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.</i></p>
60/113,687	24 December 1998 (24.12.98)	US					
09/468,399	20 December 1999 (20.12.99)	US					
<p>(54) Title: COMPOSITIONS OF PENTAFLUOROPROPANE AND DICHLOROTRIFLUOROETHANE</p> <p>(57) Abstract</p> <p>Compositions of 1,1,1,3,3-pentafluoropropane and 1,1-dichloro-2,2,2-trifluoroethane are provided. The compositions of the invention are environmentally desirable for use as refrigerants, aerosol propellants, blowing agents for polymer foam, heat transfer media, gaseous dielectrics and solvents.</p>							

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**COMPOSITIONS OF PENTAFLUOROPROPANE AND
DICHLOROTRIFLUOROETHANE**

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Field of the Invention

The present invention relates to mixtures of 1,1,1,3,3-pentafluoropropane (“HFC-245fa”) and 1,1-dichloro-2,2,2-trifluoroethane (“HCFC-123”). More particularly, the invention provides compositions of HFC-245fa and HCFC-123 that are environmentally desirable for use as refrigerants, in centrifugal chillers, aerosol propellants, metered dose inhalers, fire extinguishers, blowing agents for polymer foam, heat transfer media, gaseous dielectrics, and solvents.

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Background of the Invention

Fluorocarbon based fluids have found widespread use in industry in a number of applications, including as refrigerants, aerosol propellants, blowing agents, heat transfer media, and gaseous dielectrics. Because of the suspected environmental problems associated with the use of some of these fluids, it is desirable to use fluids of lesser ozone depletion potential such as hydrofluorocarbons, (“HFC’s”) and/or hydrochlorofluorocarbons (“HCFC’s”).

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Thus, the use of fluids that do not contain CFC’s or contain HCFC’s instead of CFC’s is desirable. Additionally, it is known that the use of single component fluids or azeotropic mixtures, which mixtures do not fractionate on boiling and evaporation, is desirable. However, the identification of new, environmentally safe, azeotropic mixtures is complicated due to the fact that it is difficult to predict azeotrope formation.

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The art continually is seeking new fluorocarbon based mixtures that offer alternatives, and are considered environmentally safe substitutes, for CFC’s and HCFC’s. Of particular interest are mixtures containing a fluorocarbon and

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hydrochlorocarbon both of low ozone depletion potentials; it is these mixtures that are the subject of this invention.

Description of the Invention and Preferred Embodiments

5 This invention provides azeotrope-like and nonazeotrope-like compositions of HFC-245fa and HCFC-123. The compositions of the invention provide environmentally desirable for currently used CFC's and HCFC's since HFC-245fa and HCFC-123 have zero and very low ozone depletion potentials, respectively. Additionally, the compositions of the invention exhibit characteristics that make the
10 compositions better CFC and HCFC substitutes than either HFC-245fa or HCFC-123 alone.

One embodiment of the invention provides azeotrope-like compositions comprising effective amounts of HFC-245fa and HCFC-123. By "effective amounts"
15 is meant the amount of each component that, on combination with the other component, results in the formation of an azeotrope-like composition. More specifically, the invention provides azeotrope-like compositions preferably of from about 90 to about 99 weight percent HFC-245fa and from about 10 to about 1 weight percent HCFC-123 having a boiling point of $15^{\circ}\text{C} \pm 2$, preferably $\pm 1^{\circ}\text{C}$, at 760 mm.
20 The preferred, more preferred, and most preferred compositions of the invention are set forth in Table 1. The numerical ranges in Table 1 are to be understood to be prefaced by the term "about".

Table 1

Components	Preferred (wt %)	More Preferred (wt %)	Most Preferred (wt %)
HFC-245fa	90 – 99	94 - 99	97- 99
HCFC-123	10 – 1	6 – 1	3 - 1

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For purposes of this invention, azeotrope-like compositions are compositions that behave like azeotropic mixtures. From fundamental principles, the thermodynamic state of a fluid is defined by pressure, temperature, liquid

composition, and vapor composition. An azeotropic mixture is a system of two or more components in which the liquid composition and vapor composition are equal at the state pressure and temperature. In practice, this means that the components of an azeotropic mixture are constant boiling and cannot be separated during a phase
5 change.

Azeotrope-like compositions behave like azeotropic mixtures, i.e., are constant boiling or essentially constant boiling. In other words, for azeotrope-like compositions, the composition of the vapor formed during boiling or evaporation is
10 identical, or substantially identical, to the original liquid composition. Thus, with boiling or evaporation, the liquid composition changes, if at all, only to a minimal or negligible extent. This is to be contrasted with non-azeotrope-like compositions in which, during boiling or evaporation, the liquid composition changes to a substantial degree. All azeotrope-like compositions of the invention within the indicated ranges
15 as well as certain compositions outside these ranges are azeotrope-like.

The azeotrope-like compositions of the invention may include additional components that do not form new azeotropic or azeotrope-like systems, or additional components that are not in the first distillation cut. The first distillation cut is the first
20 cut taken after the distillation column displays steady state operation under total reflux conditions. One way to determine whether the addition of a component forms a new azeotropic or azeotrope-like system so as to be outside of this invention is to distill a sample of the composition with the component under conditions that would be expected to separate a nonazeotropic mixture into its separate components. If the
25 mixture containing the additional component is nonazeotropic or nonazeotrope-like, the additional component will fractionate from the azeotropic or azeotrope-like components. If the mixture is azeotrope-like, some finite amount of a first distillation cut will be obtained that contains all of the mixture components that is constant boiling or behaves as a single substance.

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It follows from this that another characteristic of azeotrope-like compositions is that there is a range of compositions containing the same components in varying proportions that are azeotrope-like, or constant boiling. All such compositions are intended to be covered by the terms "azeotrope-like" and "constant boiling". As an
 5 example, it is well known that at differing pressures, the composition of a given azeotrope will vary at least slightly as does the boiling point of the composition. Thus, an azeotrope of A and B represents a unique type of relationship, but with a variable composition depending on temperature and/or pressure. It follows that, for azeotrope-like compositions, there is a range of compositions containing the same
 10 components in varying proportions that are azeotrope-like. All such compositions are intended to be covered by the term azeotrope-like as used herein.

In another embodiment of the invention, nonazeotrope-like compositions are provided which compositions comprise HFC-245fa and HCFC-123 and which have a
 15 vapor pressure of about 18 psia to about 19 psia at 20° C. Preferably, the compositions of the invention comprise from about 90 to about 99 weight percent HFC-245fa and from about 10 to about 1 weight percent HCFC-123a. The preferred, more preferred, and most preferred compositions of this embodiment are set forth in Table 2. The numerical ranges in Table 2 are to be understood to be prefaced by the
 20 term "about."

Table 2

Components	Preferred (wt %)	More Preferred (wt %)	Most Preferred (wt %)
HFC-245fa	90-99	94-99	97-99
HCFC-123	10-1	6-1	3-1

The compositions of the invention meet the need in the art for CFC/HCFC
 25 mixtures that have a low ozone depletion potential and are negligible contributors to greenhouse global warming, are nonflammable, and have an appropriate compressor discharge temperature. Additionally, the compositions of the invention offer superior refrigeration capacity when compared to such fluids as HFC-245fa or HCFC-123

alone. Further, because the azeotrope-like compositions of the invention exhibit constant vapor pressure characteristics and relatively minor composition shifts as the liquid mixture is evaporated, the azeotrope-like composition of the invention are comparable to a constant boiling single component refrigerant or an azeotropic
5 mixture refrigerant.

In a process embodiment, the compositions of the invention may be used in a method for producing refrigeration that comprises condensing a refrigerant comprising the azeotrope-like or nonazeotrope-like compositions of this invention and
10 thereafter evaporating the refrigerant in the vicinity of a body to be cooled. In yet another process embodiment, the compositions of the invention may be used in a method for heating that comprises condensing a refrigerant comprising the azeotrope-like or nonazeotrope-like compositions of the invention in the vicinity of a body to be heated and thereafter evaporating the refrigerant.

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In another embodiment, the compositions of the invention may be used in centrifugal chillers. By "centrifugal chillers" is meant refrigeration equipment that uses centrifugal compression to compress the refrigerant. The invention provides a method for producing refrigeration using a centrifugal compressor comprising
20 compressing a refrigerant comprising the azeotrope-like or nonazeotrope-like compositions of the invention and thereafter evaporating the refrigerant in the vicinity of a body to be cooled

In still another embodiment, the compositions of the invention may be used in
25 a method for producing foam comprising blending a heat plasticized resin with a volatile blowing agent comprising the azeotrope-like or nonazeotrope-like compositions of the invention and introducing the resin/volatile blowing agent blend into a zone of lower pressure to cause foaming.

30 In another process embodiment, the compositions of the invention are used in a method for producing polyurethane and polyisocyanurate foams. Any of the

methods well known in the art such as those described in "Polyurethanes Chemistry and Technology," Volumes I and II, Saunders and Frisch, 1962, John Wiley and Sons, New York, NY. In general, the method comprises preparing polyurethane or polyisocyanurate foams by combining an isocyanate, a polyol or mixture of polyols, a blowing agent or mixture of blowing agents, and other materials such as catalysts, surfactants, and optionally, flame retardants, colorants, or other additives. The blowing agent or agents employed shall be a volatile mixture of the azeotrope-like or nonazeotrope-like compositions of the present invention.

10 It is convenient in many applications to provide the components for polyurethane or polyisocyanurate foams in preblended formulations. Most typically, the foam formulation is preblended into two components. The isocyanate and optionally certain surfactants and blowing agents comprise the first component, commonly referred to as the "A" component. The polyol or polyol mixture, surfactant, catalysts, blowing agents, flame retardant, and other isocyanate reactive components comprise the second component, commonly referred to as the "B" component. Accordingly, polyurethane and polyisocyanurate foams are readily prepared by bringing together the A and B side components either by hand mix for small preparations and, preferably, machine mix techniques to form blocks, slabs, laminates, pour-in-place panels and other items, spray applied foams, froths, and the like. Optionally, other ingredients such as fire retardants, colorants, auxiliary blowing agents, water, and even other polyols can be added as a third stream to the mix head or reaction site. Most conveniently, however, they are all incorporated into one B component as described above.

25 It is also possible to produce thermoplastic foams using the compositions of the invention. For example, conventional foam polyurethanes and isocyanurate formulations may be combined with the azeotrope-like or nonazeotrope-like composition in a conventional manner to produce rigid foams.

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Azeotrope-like and nonazeotrope-like mixtures containing HFC-245fa are particularly suitable as foam blowing agents since foams blown with HFC-245fa have been found to possess low relative initial and aged thermal conductivity and good dimensional stability at low temperatures. Of particular interest are those mixtures
5 that contain HFC-245fa and other zero or low ozone depletion HFC's and/or HCFC's.

The compositions of the invention may also be used as heat transfer fluids. For example, in certain refrigeration systems, it is desirable to operate the system at a specific temperature. However, maintaining the desired temperature may require
10 either the addition or removal of heat. Thus, a secondary heating loop containing an appropriate heat transfer fluid may be added. The heat transfer fluid absorbs heat in one part of the cycle and transfers the heat to another part of the cycle without changing state, when the heat transferred is sensible, or by changing state, when the heat transferred is latent.

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In another embodiment, the mixtures and compositions of this invention may be used as propellants in sprayable compositions, either alone or in combination with known propellants. The sprayable composition comprises, consists essentially of, and consists of a material to be sprayed and a propellant comprising, consisting essentially
20 of, and consisting of a mixture or composition of the invention. Inert ingredients, solvents, and other materials may also be present in the sprayable mixture. Preferably, the sprayable composition is an aerosol. Suitable materials to be sprayed include, without limitation, cosmetic materials such as deodorants, perfumes, hair sprays, cleansers, and polishing agents as well as medicinal materials such as anti-
25 asthma and anti-halitosis medications.

The compositions of the invention may also be used in a method of dissolving contaminants or removing contaminants from the surface of a substrate, which method comprises the step of contacting the substrate with the compositions of the present
30 invention. In another embodiment, the compounds and mixtures of the present invention may also be used as fire extinguishing agents.

The components of the composition of the invention are known materials that are commercially available or may be prepared by known methods. Preferably, the components are of sufficiently high purity so as to avoid the introduction of adverse
5 influences on the properties of the system.

Additional components may be added to tailor the properties of the compositions of the invention as needed. By way of example, oil solubility aids may be added in the case in which the compositions of the invention are used as
10 refrigerants.

The present invention is more fully illustrated by the following non-limiting examples.

15

Examples

Example 1

An ebulliometer consisting of a vacuum-jacketed tube with a condenser on top was used. About 11.3 g HFC-245fa were charged to the ebulliometer and HCFC-123 was added in small, measured increments. The temperature was measured using a
20 platinum resistance thermometer. From about 0 to about 0.8 weight percent HCFC-123, the boiling point of the composition did not change. Therefore, the composition boils as a constant-boiling composition over this range.

Example 2

25 An ebulliometer consisting of a vacuum-jacketed tube with a condenser on top was used. About 16.7 g HFC-245fa were charged to the ebulliometer and HCFC-123 was added in small, measured increments. The temperature was measured using a platinum resistance thermometer. From about 0 to about 1.7 weight percent
30 HCFC-123, the boiling point of the composition changed by only 0.02°C. Therefore, the composition boils as a constant-boiling composition over this range.

Example 3

This example demonstrates that constant-boiling blends of HFC-245fa and HCFC-123 have certain advantages compared to either HFC-245fa or HCFC-123 alone. The theoretical performance of a refrigerant at specific operating conditions
5 can be estimated from the thermodynamic properties of the refrigerant using standard refrigeration cycle analysis techniques. See, e.g., R.C. Downing Fluorocarbon Refrigerants Handbook, Prentice Hall (1988). The coefficient of performance, COP, is a universally accepted measure especially useful in representing the relative thermodynamic efficiency of a refrigerant in a specific heating or cooling cycle
10 involving evaporation or condensation of a refrigerant. This term expresses the ratio of useful refrigeration to the energy applied by the compressor in compressing the vapor. The capacity of a refrigerant represents the volumetric efficiency of the refrigerant. This value expresses the capability of a compressor to pump quantities of heat for a given volumetric flow rate of refrigerant. In other words, given a specific
15 compressor, a refrigerant with a higher capacity will deliver more cooling or heating power.

This type of calculation is performed for an air conditioning cycle in which the condenser temperature was 110° F and the evaporator temperature was 35° F.
20 Compression efficiency of 85 %, superheat of 20° F, and a subcooling of 10° F were assumed. Calculations were performed for various combinations of HFC-245fa and HCFC-123 and for HFC-245fa and HCFC-123 as single components. Table 3 lists the COP and capacities of the compositions of the invention relative to HFC-245fa and HCFC-123.

25

Table 3
Thermodynamic Performance

Refrigerant	COP	Capacity (cfm)
HCFC-123	4.85	540
HFC-245fa/HCFC-123 (99/1 wt %)	4.76	833
HFC-245fa/HCFC-123 (97/3 wt %)	4.76	833
HFC-245fa/HCFC-123 (94/6 wt %)	4.77	831
HFC-245fa/HCFC-123 (90/10 wt %)	4.77	829
HFC-245fa	4.70	812

As Table 3 illustrates, the compositions of the invention are better than either pure component HFC-245fa or HCFC-123 in terms of refrigeration capacity, and are comparable in terms of COP.

Example 4

40 g of each of the azeotrope-like compositions given in Table 1 are charged into individual 200 cc sealed vessels containing 3 g on Dow styrene 685D. The vessels are placed in a 250° F oven overnight. Twenty-four hours later, the vessels are removed from the oven and rapidly depressurized. The resulting foams are inspected and found to be of good quality.

Example 5

This example illustrates the use of preferred azeotrope-like compositions of the invention to clean (deflux) printed wiring boards and printed wiring assemblies. A commercial rosin based flux viz. Kenco 885 (manufactured by Kenco Industries, Inc.) is used in this test.

In the experiment FR-4 epoxy coupons cut to a size of 1"X2.25" are used for flux and subsequent cleaning. Prior to fluxing all specimen are precleaned to ensure very low levels of contamination before fluxing. The contamination is measured by measuring conductivity of the wash solution (in equivalent micrograms of sodium

chloride) per square inch of the boards using a conductivity bridge. (See U.S. Patent No. 4,816,175). Using this technique, it is determined that all specimens are precleaned to 0.05 micrograms or less of sodium chloride equivalents.

5 A measured amount of Kenco 885 flux is applied to each of the coupons. The coupons are air dried and dried at 90 C for 5 minutes and baked at 230 C for 1 minute. This procedure mimics the Hollis wave solder machine. The amount of ionic materials left in the board after the drying process is of the same order of magnitude as in a wave solder machine.

10

 These fluxed coupons are then cleaned in the boiling solvents for two minutes, after which the amount of ionics is washed off by a 75/25 by weight water/isopropanol (IPA) mixture for 24 hours. The conductivity of the water/IPA mixture is measured as described previously.

15

 The cleaning study results show that the solvent (245fa/123) mixtures of the invention remove ionic impurities much more efficiently than 245fa alone.

What is claimed is:

1. Azeotrope-like compositions consisting essentially of an effective amount of 1,1,1,3,3-pentafluoropropane and 1,1-dichloro-2,2,2-trifluoroethane which
5 compositions boil at about $15^{\circ}\text{C} \pm 2^{\circ}\text{C}$ at 760 mm Hg.
2. The compositions of claim 1 consisting essentially of from about 99 to about 90 weight percent 1,1,1,3,3-pentafluoropropane and from about 1 to about 10 weight percent 1,1-dichloro-2,2,2-trifluoroethane.
10
3. The compositions of claim 1 consisting essentially of from about 99 to about 94 weight percent 1,1,1,3,3-pentafluoropropane and from about 1 to about 6 weight percent 1,1-dichloro-2,2,2-trifluoroethane.
- 15 4. The compositions of claim 1 consisting essentially of from about 99 to about 97 weight percent 1,1,1,3,3-pentafluoropropane and from about 1 to about 3 weight percent 1,1-dichloro-2,2,2-trifluoroethane.
5. Compositions comprising 1,1,1,3,3-pentafluoropropane and 1,1-dichloro-
20 2,2,2-trifluoroethane having a vapor pressure of from about 18 psia to about 19 psia at 20°C .
6. The compositions of claim 5 consisting essentially of 1,1,1,3,3-pentafluoropropane and 1,1-dichloro-2,2,2-trifluoroethane.
25
7. A method for producing refrigeration comprising condensing a refrigerant comprising the azeotrope-like compositions of claims 1, 2, 3 or 4 and thereafter evaporating the refrigerant in the vicinity of a body to be cooled.

8. A method for producing refrigeration comprising condensing a refrigerant comprising the compositions of claims 5 or 6 and thereafter evaporating the refrigerant in the vicinity of a body to be cooled.
- 5 9. A method for producing heating comprising condensing a refrigerant comprising the azeotrope-like compositions of claims 1, 2, 3, or 4 in the vicinity of a body to be heated and thereafter evaporating the refrigerant.
- 10 10. A method for producing heating comprising condensing a refrigerant comprising the compositions of claims 5 or 6 in the vicinity of a body to be heated and thereafter evaporating the refrigerant.
- 15 11. A method for producing polyurethane and polyisocyanurate foams comprising reacting and foaming a mixture of ingredients that will react to form the polyurethane and polyisocyanurate foams in the presence of a volatile blowing agent comprising the azeotrope-like compositions of claims 1, 2, 3 or 4.
- 20 12. A method for producing polyurethane and polyisocyanurate foams comprising reacting and foaming a mixture of ingredients that will react to form the polyurethane and polyisocyanurate foams in the presence of a volatile blowing agent comprising the compositions of claims 5 or 6.
- 25 13. A premix of a polyol and a blowing agent comprising the azeotrope-like compositions of claims 1, 2, 3 or 4.
14. A premix of a polyol and a blowing agent comprising the compositions of claims 5 or 6.
- 30 15. A method for producing foam comprising blending a heat plasticized resin with a volatile blowing agent comprising the azeotrope-like compositions of claims 1,

2, 3, or 4 and introducing the resin/volatile blowing agent blend into a zone of lower pressure to cause foaming.

16. A method for producing foam comprising blending a heat plasticized resin
5 with a volatile blowing agent comprising the compositions of claims 5 or 6 and introducing the resin/volatile blowing agent blend into a zone of lower pressure to cause foaming.

17. A method for heating or cooling a body comprising passing the azeotrope-like
10 compositions of claims 1, 2, 3, or 4 near the body so that the compositions transfer heat to or from the body.

18. A method for heating or cooling a body comprising passing the compositions
15 of claims 5 or 6 near the body so that the compositions transfer heat to or from the body.

19. A method for producing refrigeration using a centrifugal compressor
comprising compressing a refrigerant and thereafter evaporating the refrigerant in the
vicinity of a body to be cooled, wherein the refrigerant comprises the azeotrope-like
20 compositions of claims 1, 2, 3, or 4.

19. A method for producing refrigeration using a centrifugal compressor
comprising compressing a refrigerant and thereafter evaporating the refrigerant in the
vicinity of a body to be cooled, wherein the refrigerant comprises the compositions of
25 claims 5 or 6.

20. An aerosol composition comprising a propellant and a material to be sprayed
wherein the propellant comprises the azeotrope-like composition of claims 1, 2, 3, or
4.

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21. An aerosol composition comprising a propellant and a material to be sprayed wherein the propellant comprises the composition of claims 5 or 6.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/30411

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C09K5/04 C09K3/30 C08J9/14		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 C09K C08J		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 13335 A (DU PONT) 18 May 1995 (1995-05-18) the whole document	1-21
A	US 5 295 357 A (KANEKO MASATO) 22 March 1994 (1994-03-22) claim 1	1,7
A	US 5 683 974 A (SWAN ELLEN LOUISE ET AL) 4 November 1997 (1997-11-04) the whole document	1
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Date of the actual completion of the international search 13 April 2000		Date of mailing of the international search report 03/05/2000
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PCT/US 99/30411

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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