

AZEOTROPE-LIKE SOLVENT BLENDS EXHIBITING LOW GLOBAL WARMING POTENTIAL AND METHODS OF USE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority of provisional patent application Serial No. 63/487,906 filed on March 2, 2023 in the name of Trenessa Rioux, and entitled "AZEOTROPE-LIKE SOLVENT BLENDS EXHIBITING LOW GLOBAL WARMING POTENTIAL AND METHODS OF USE".

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] The present invention concerns solvent-based cleaning compositions (sometimes herein referred to as "blends") of the type used in industrial processes for cleaning a wide variety of items including metals and plastics in the metalworking, electronics and other industries. These solvent based cleaning compositions are non-flammable and azeotrope-like, are composed of non-ozone-depleting, low global warming potential ingredients, and having highly effective cleaning power. The solvent blends of the present invention also find use as a carrier liquid for lubricants and the like.

Description of Related Art

[0003] Solvent blends are used in industrial processes for cleaning a wide variety of soiling substances and residues (below sometimes referred to as "soils" or "soiling substances"). The electronics industry typically cleans fluxes, solder pastes, adhesives and coatings from a variety of devices before and after assembly of components. Such devices may comprise one or more of a wide range of materials comprising metal, ceramic and synthetic polymer (plastic) substrates and components. Metal working operations must remove lubricant oils and soaps, grinding media and greases from metal surfaces. Many of these soils are very difficult to strip from metal surfaces, especially with non-aqueous cleaners.

[0004] Of special interest are non-flammable blends of solvents that provide a cleaning solvent which can be used safely in aerosol packages, or as wiping fluids or in bulk cleaning tanks, for example, in vapor degreasing ("VDG") units. Typically, these cleaning solvents comprise halogenated compounds that are either non-flammable themselves or can be rendered non-flammable in a mixture with other halogenated compounds. For example, it

is known to use chlorinated hydrocarbons, such as flammable trans-dichloroethylene (TDCE), as the high solvency component with fluorinated components that serve to render the cleaning solvent blend non-flammable. In addition, and especially for VDG applications, the cleaning solvent blend should be an azeotrope or exhibit azeotrope-like behavior and be non-flammable, so that the vapor is also non-flammable. Therefore, it is highly desirable that the azeotrope not significantly fractionate after distillation, condensation, and re-mixing, as happens in a vapor degreaser. That is, the component ratios should be nearly the same or at least not drastically changed in the boil sump as in the rinse sump in a VDG; or boil flask and receiver over the course of a full distillation.

[0005] The industry seeks to maximize the cleaning power of its products, often defined as the Kauri-Butanol index ("KB value"). A high KB value indicates high cleaning power for a solvent component or solvent blend. In order to attain a high KB value, the concentration of TDCE, or other high KB value components in the blend is made as high as is feasible. However, the solvent blend becomes more difficult to render non-flammable as the amount of the high KB value component in the composition is increased. A significant advance in the art was made by Dupont Corporation with the introduction of an azeotrope-like blend of 4% by weight of methylperfluoroheptene (MPHE) ethers, 0.8% Vertrel XF and 95.2% TDCE, offered as Opteon SF79 by Chemours. This is currently the highest concentration of TDCE in a commercial product. The KB value of this product is 100. However, the high TDCE concentration adversely affects flammability, that is, the Opteon SF79 solvent is more flammable than desired.

[0006] Robin et al. Patent Application Publication US 2016/0326468 A1, published on November 10, 2016, discloses in paragraph [0010] a composition comprising from 0.1 to 8 weight percent methylperfluoroheptene ethers, from 90 to 99 weight percent trans-1,2-dichloroethylene and from 0.6 to 2 weight percent of a hydrofluorocarbon (HFC) selected from a very large group which includes heptafluorocyclopentane.

[0007] U.S. Patent 10,669,502 to D. Ikeda et. al. issued June 2, 2020 discloses 65-80% of TDCE, 5-25% of a low boiling (40-65° C) HFE and 5-25% of a high boiling (70-120° C) HFE as cleaning and carrier fluid compositions.

[0008] U.S. Patent 10,828,579 to R. Singh issued November 10, 2020 discloses aerosol compositions of trans and cis 1-chloro-2,3,3-trifluoro-1-propene (HCFO 1233yd E&Z) along with a large group of cosolvents.

[0009] U.S. Patent Publication 2022/0073804 published March 10, 2022 to H. Mitsuoka discloses an azeotrope of TDCE (34.5%) and HCFO1233ydZ (65.5%).

[0010] U.S. Provisional Patent Application Serial No. 63/351,969 (Attorney Docket MCC0125US) discloses azeotropic solvent blends of 70-95.7% TDCE, 3.8-15% heptafluorocyclopentane and 0.5-15% 1-chloro-2,3,3-trifluoro-1-propene.

[0011] In addition to maximizing cleaning power and reducing flammability, the industry seeks cleaning products with minimal environmental impact. Ideally, cleaning products should have zero-ozone depleting potential and negligible global warming potential.

[0012] Hydrochlorofluorocarbons with high ozone depleting potential have been replaced in the market with non-ozone depleting hydrofluorocarbons. Today, many hydrofluorocarbons are also being replaced due to their high global warming potential. For example, HFC-43-10mcc, commonly known as Vertrel XF has a Global Warming Potential ("GWP") of 1640.

[0013] The Global Warming Potential (GWP) was developed to allow comparisons of the global warming impacts of different gases. Specifically, it is a measure of how much energy the emissions of 1 ton of a gas will absorb over a given period of time, relative to the emissions of 1 ton of carbon dioxide (CO₂). The larger the GWP, the more that a given gas warms the Earth compared to CO₂ over that time period. The time period usually used for GWPs is 100 years. GWPs provide a common unit of measure, which allows analysts to add up emissions estimates of different gases. Hydrofluoroethers (HFE), hydrofluoroolefins (HFO) and hydrochlorofluoroolefins (HCFO) have low global warming potentials and are therefore preferable ingredients in cleaning products.

SUMMARY OF THE INVENTION

[0014] The present invention concerns low flammability, low global warming potential cleaning solvent compositions which exhibit azeotrope-like behavior. The azeotrope-like behavior enables effective use of these solvent compositions (sometimes herein referred to as solvent blends or blends) in vapor degreaser operations. The cleaning solvent compositions of the present invention are substantially non-fractionating or undergo only limited fractionation upon distillation, which is important for both the efficient and safe operation of cleaning operations and safety of various solvent packages such as bulk solvent, and solvent aerosol, wipes, and pump sprays. The solvent compositions of the present invention are also useful in other applications, such as serving as carrier liquids for lubricants or other materials, for example, the application of lubricants in manufacturing operations.

[0015] The present invention provides solvent blends comprising from about 40 wt % to about 90 wt % trans-dichloroethylene, a monochlorotrifluoropropene, a hydrofluoroether

and, optionally, a C1 to C3 alcohol. One or both of a suitable surfactant and a suitable cosolvent may be added in amounts which do not significantly adversely affect the non-flammable, azeotrope-like and effective cleaning capability of the solvent blends.

[0016] For example, one embodiment of a solvent blend of the present invention comprises 59-80% trans-dichloroethylene; 11-23% of a monochlorotrifluoropropene, such as one or more of those described in U.S. Patent 10,828,579 column at 5, lines 1-17; 5-20% high boiling hydrofluoroether (HFE) as described in claim 2 of U.S. Patent 10,669,502; and 0-5% of a C1-C3 alcohol. The solvent blends of the present invention may, in certain embodiments, contain other ingredients such as the surfactants and cosolvents described below as well as other ingredients of a character and in amounts which maintain the azeotrope-like, low global warming potential and cleaning efficacy properties of the solvent blends. Alternatively, the solvent blends of the present invention may be limited to ("consisting of") only the claimed ingredients or the claimed ingredients plus ingredients which do not affect the basic characteristics ("consisting essentially of") the invention.

[0017] The monochlorotrifluoropropene may be selected, for example, from the group consisting of one or more of transCF₃CH=CClH (1233zdE); cisCF₃CH=CClH (1233zdZ); transCHF₂CF=CClH (1233ydE); cisCHF₂CF=CClH (1233ydZ); transCHF₂CH=CClF (1233zbE); cisCHF₂CH=CClF (1233zbZ); transCHF₂CCl=CHF (1233xeE); cisCHF₂CCl=CHF (1233xeZ); CH₂FCCl=CF₂ (1233x0); transCHFC1CF=CFH (1233yeE); cisCHFC1CF=CFH (1233yeZ); CH₂C1CF=CF₂ (1233yc); CF₂C1CF=CH₂ (1233xf) and two or more thereof.

[0018] For example, the hydrofluoroether may be selected from the group consisting of one or more of ethoxynonafluorobutane, 1,1,2,3,3,3-hexafluoropropyl-2,2,2-trifluoroethyl ether, 1,1,2,2-tetrafluoroethyl-2,2,3,3,3-pentafluoropropyl ether, 1,1-difluoroethyl-2,2,3,3-tetrafluoropropyl ether, 1,1,2,3,3,3-hexafluoropropyl-2,2,3,3,3-pentafluoropropyl ether, 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether, 1,1,2,3,3,3-hexafluoropropyl-2,2,3,3-tetrafluoropropyl ether, and 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane and two or more thereof.

[0019] Still other aspects of the present application provide solvent compositions exhibiting azeotrope-like properties and comprising:

from about 71 to about 75 wt % trans-dichloroethylene (TDCE), from about 15 to about 19 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and from about 7 to about 10 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300);

from about 85 to about 95 wt % trans-dichloroethylene (TDCE), from about 1 to about 5 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and from about 1 to about 5 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300);

about 90 wt % trans-dichloroethylene (TDCE), about 5 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and about 5 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300).

from about 59 to about 70 wt % trans-dichloroethylene (TDCE), from about 10 to about 25 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300), from about 11 to about 18 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300) and from about 1 to about 5 wt % ethanol;

about 63 wt % trans-dichloroethylene (TDCE), about 20 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300), about 15 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300) and about 2 wt % ethanol;

from about 40 to about 60 wt % trans-dichloroethylene (TDCE), from about 15 to about 40 wt % of 1,1,2,2 tetrafluoroethyl 2,2,2-triethyl ether (AE3000) and from about 10 to about 25 wt % 1,1,1,2,3,3-hexafluoro-3-methoxy propane (HFE-356);

from about 40 to about 60 wt % trans-dichloroethylene (TDCE), from about 11 to about 21 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and from about 20 to about 40 wt % 1,1,1,2,3,3-hexafluoro-3-methoxy propane (HFE-356); and

about 53 wt % trans-dichloroethylene (TDCE), about 11 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and about 36 wt % 1,1,1,2,3,3-hexafluoro-3-methoxy propane (HFE-356).

[0020] A method aspect of the present invention provides for cleaning soiling substances from metal, ceramic and synthetic polymer articles comprising contacting one or more of the articles with the solvent composition exhibiting azeotrope-like properties as disclosed herein and removing the solvent composition from the articles.

[0021] The present invention overcomes or at least ameliorates the problems of the prior art such as U.S. Patent 10,669,502. This is accomplished by using a monochlorotrifluoropropene (HCFO) in place of the lower boiling hydrofluoroethers specified in U.S. Patent 10,669,502, so that the concentration of TDCE can be maintained while the KB value is substantially increased due to the inherent higher KB value of HCFOs. In addition, the superior flame suppressing characteristics of HCFOs allow the optional introduction C1-C3 alcohols into the solvent blends of the present invention which further increases the KB value of the blends without rendering the blends flammable while keeping the TDCE in lower

weight percentage. This can be critical in applications such as removing highly polar / ionic contaminants in so-called “no-clean” fluxes used in the electronic industry. Lower percentage of TDCE sometimes are needed when compatibility of plastic substrates are sought for, because higher TDCE level can affect the plastic substrates compatibility.

[0022] One embodiment of a cleaning solvent composition of the present invention comprises from about 59 to about 70 weight percent trans-dichloroethylene (TDCE), from about 10 to about 25 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300), from about 11 to about 18 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300) and from about 1 to about 5 wt % ethanol. The KB value of this blend is 99.

[0023] A second embodiment of a cleaning solvent composition of the present invention comprises from about 70 to about 80 weight percent trans-dichloroethylene (TDCE), from about 11 to about 21 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and from about 5 to about 15 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300). The KB value of this blend is 99.

[0024] A third embodiment of a cleaning solvent composition of the present invention comprises from about 40 to about 60 weight percent trans-dichloroethylene (TDCE), from about 11 to about 21 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and from about 20 to about 40 wt % 1,1,1,2,3,3-hexafluoro-3-methoxy propane (HFE-356). The KB value of this blend is 57.

[0025] A fourth embodiment of a cleaning solvent composition of the present invention comprises from about 40 to about 60 weight percent trans-dichloroethylene (TDCE), from about 15 to about 40 wt % of 1,1,2,2-tetrafluoroethyl 2,2,2-triethyl ether (AE3000) and from about 10 to about 25 wt % 1,1,1,2,3,3-hexafluoro-3-methoxy propane (HFE-356). The KB value of this blend is 58.

[0026] A fifth embodiment of a cleaning solvent composition of the present invention comprises from about 85 to about 95 wt % trans-dichloroethylene (TDCE), from about 1 to about 5 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and from about 1 to about 5 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300). The KB value of this blend is 115.

[0027] Yet another embodiment of a cleaning solvent composition of the present invention comprises any one of the aforementioned embodiments with the addition of a surfactant in a concentration of about 0.1 to about 3 weight percent. Suitable surfactants include, but are not limited to Rhodafac RS-710 (80-90% Polyoxyethylene Tridecyl Ether Phosphate [CAS#9046-01-9], 15-20% Alcohol Ethoxylate [CAS#78330-21-9], 1-5%

Phosphoric Acid [CAS#7664-38-2], <1% Water [CAS#7732-18-5]), Tergitol 15-S-3 (C12-14 Secondary ethoxylated alcohols), Steposol (N,N-dimethyl-9-decenamide, [MET10U]).

[0028] Still another embodiment of a cleaning solvent composition of the present invention comprises any one of the aforementioned solvent blends of the present invention with the addition of a cosolvent in an amount of about 1 to about 50 weight percent of the weight of the other ingredients of the solvent blend. This embodiment of the present invention is below referred to as "the high cosolvent blend". In this embodiment the boil sump of a vapor degreasing unit is supplied with the high cosolvent blend and the cosolvent would not distill over to the rinse sump. Suitable cosolvents include but are not limited to Steposol (N,N-dimethyl 9-decenamide, [MET10U]), Rhodafac RS-710 (80-90% Polyoxyethylene Tridecyl Ether Phosphate [CAS#9046-01-9], 15-20% Alcohol Ethoxylate [CAS#78330-21-9], 1-5% Phosphoric Acid [CAS#7664-38-2], <1% Water [CAS#7732-18-5]) Benzyl Alcohol, Hexylene Glycol.

[0029] Unless otherwise specifically stated, or clear from the context, all percentages of a given component, whether expressed as "wt %", "weight %", "weight percent" or otherwise, are percent by weight of the component in the solvent blend, based on the total weight of the solvent blend.

[0030] As used herein, the term "azeotrope-like" behavior or characteristics or language of similar import used with reference to the cleaning solvent blends of the present invention means that while the solvent blends may not exhibit perfect azeotropic characteristics (although some of the blends of the present invention may do so), the changes in composition after repeated distillation steps are small or limited, that is, not more than 20 wt % of the initially present quantity of each component of the blend over a sustained distillation (evaporation and condensation) period of at least 5 hours. Generally, the term "azeotrope-like composition" means a constant boiling, or substantially constant boiling liquid admixture of two or more substances that behaves under distillation as if or nearly as if it were a single substance. That is, the vapor produced by distillation of the liquid has at least approximately the same composition (within the 20 wt % change as described above) as the liquid from which it was distilled. Stated otherwise, there is no substantial composition change as the admixture is distilled. Further, an azeotrope-like composition may be characterized as a composition having a boiling point temperature of less than the boiling point of each pure component of the composition.

[0031] To illustrate, the azeotrope-like behavior of one of the solvent blend embodiments of the present invention, refer to Example 5 below. The TDCE component is

initially present in the amount of 75 wt % of the blend and even after the ninth stage of the fractional distillation, when the remaining blend was only 24 wt % of the starting amount, the TDCE is present in the amount of 75.44 wt %. The weight percent of TDCE removed by the fractional distillation is calculated as follows: $(75.44-75)/75 \times 100 = 0.58$ weight percent. This illustrates the azeotrope-like behavior of this solvent blend.

[0032] The solvent compositions of the present invention may contain other ingredients, such as surfactants and cosolvents as noted above, provided that the type and quantity of such other ingredients do not significantly adversely affect the low global warming potential or the azeotrope-like characteristics or the cleaning efficacy of the compositions. That is, the solvent blends of the present invention may either comprise, or consist of, or consist essentially of the specified ingredients. In some cases, the solvent blends may consist of only the specified ingredients except for trace impurities found in commercially available ingredients used to make the solvent blends of the present invention. A propellant may be used to deliver the solvent compositions of the present invention. Inasmuch as such propellants evaporate they do not affect the low global warming potential characteristics, or the azeotrope-like characteristics or the cleaning efficacy of the solvent compositions.

BRIEF DESCRIPTION OF THE DRAWINGS

[0033] Figure 1 is a schematic view in elevation of a bench top simulation of a standard 2-sump vapor degreaser comprising a dual bulb apparatus of the type used to develop the data dual bulb distillation data described below; and

[0034] Figures 2-11 are graphs showing changes in concentration of the ingredients of the identified solvent blends during dual bulb or fractional distillation, as indicated.

DETAILED DESCRIPTION OF THE INVENTION AND SPECIFIC EMBODIMENTS THEREOF

[0035] The following abbreviations, trademarks and trade names have the following meanings, whether used in the singular or plural form.

"TDCE" or "Trans". Trans-Dichloroethylene. Chemical Abstracts Number ("CAS #") 156-60-5.

"XF". The hydrofluorocarbon, 2,3-dihydrodecafluoropentane (HFC 43-10me) [Tradename

Vertrel XF]. CAS # 1384-95-42.

“AS300”. A specific blend of cis- and trans- geometric isomers of 1-chloro-2,3,3,-trifluoropropene composed of >89% (Z)-1-chloro-2,3,3,-trifluoropropene and <10% (E)-1-chloro-2,3,3,-trifluoropropene, as supplied by AGC, Inc. Chemicals Company under the tradename “Amolea AS300”.

“SF33”. The hydrofluoroolefin, (Z)-1,1,1,4,4,4-Hexafluoro-2-butene; Tradename Opteon SF33 by Chemours Company. CAS# 692-49-9.

“HFX-110”. Methylperfluoroheptene ethers; Tradename HFX-110. CAS # Proprietary.

“HFCs”. Such as 2,3-dihydrodecafluoropentane (HFC 43-10mee) and heptafluorocyclopentane.

“HFCP”. 1,1,2,2,3,3,4-Heptafluorocyclopentane. Tradename Zeorora. CAS# 15290-77-4.

“HFEs”. Hydrofluoroethers such as 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane CAS#132182-92-4 (HFE-7300).

“Vertrel® SFR”. A blend of 67% trans-dichloroethylene, 18% 2,3-dihydrodecafluoropentane (HFC 43-10mee) ;12% heptafluorocyclopentane; 3% methanol. This material has a boiling point of 106°F (41.1°C) and is available from Chemours Corporation of Wilmington, Delaware.

“Opteon SF79”. A blend of nominally 95.2% trans-dichloroethylene, 4.0% methylperfluoroheptene ethers (HFX-110) and 0.8% 2,3-dihydrodecafluoropentane (HFC 43-10mee). This material has a boiling point of 121°F (49.4°C) and is available from Chemours Corporation of Wilmington, Delaware.

“Opteon SF80”. A blend of nominally 95.2% trans-dichloroethylene, 4.0% methylperfluoroheptene ethers (HFX-110) and 0.8% (Z)-1,1,1,4,4,4-Hexafluoro-2-butene (Opteon SF33). This material has a boiling point of 121°F (49.4°C) and is available from Chemours Corporation of Wilmington, Delaware.

“EtOH.” Ethyl alcohol.

“MeOH”. Methyl alcohol.

[0036] Figure 1 shows laboratory glassware 10 comprising a boil bulb 12 having a neck 12a which protrudes into rinse bulb 14. Neck 12a has formed therein an aperture 12b which is disposed within rinse bulb 14. A condenser 16 is fitted to rinse bulb 14 at the outlet end 14a thereof and comprises a cooling coil 18 disposed within condenser 16. A cold water inlet 18a is connected to a source of cooling water (not shown) and a cold water outlet 18b is connected to a water discharge (not shown). Boil bulb 12 is disposed upon a heating mantel 20.

[0037] In use, a solvent composition to be tested is introduced into boil bulb 12 and heated to boil the solvent composition and generate a vapor which rises to rinse bulb 14 and then into condenser 16 as indicated by arrows V1. Vapor is condensed by contact with cooling coil 18 and flows into rinse bulb 14 as indicated by arrows C1. When the condensate collected in rinse bulb 14 reaches the level of aperture 12b, the overflow solvent flows back into boil bulb 12 as indicated by arrow C2.

[0038] Standard Test Procedure. Trials were conducted in standard 2-sump vapor degreasers or in bench top simulation using a “dual bulb” apparatus of the type illustrated in Figure 1 having a standard solvent still head with collection flask and sampling port (not shown in Figure 1) on the boil flask. Samples from various locations and times are analyzed by gas chromatography using an Agilent Corporation DB-200 capillary column (trifluoropropyl methyl dimethyl siloxane stationary phase) and an FID detector. The following examples report the results of trials conducted pursuant to this Standard Test Procedure.

Comparative Example 1. Distillation of Vertrel® SFR in a Vapor Degreaser.

Composition of Vertrel SFR Over Time in Branson B-452R Degreaser								
	wt. % TDCE		wt. % HFCP		wt. % XF		wt. % MeOH	
Virgin (Drum)	67.7		12.2		17.3		2.8	
Time Distilled	Boil Sump	Rinse Sump	Boil Sump	Rinse Sump	Boil Sump	Rinse Sump	Boil Sump	Rinse Sump
1 hour	75.8	68	16.5	12.2	6.6	16.7	0.9	2.9
2 hours	76.4	67.6	16.8	12.1	5.9	17.2	0.8	3
5 hours	77.3	68.3	16.4	11.7	5.4	16.9	0.7	3
7 hours	77.3	68.3	16.5	11.7	5.3	16.9	0.7	3
9 hours	76.9	67.9	16.9	12.1	5.4	16.9	0.7	2.9
12 hours	77.9	68.3	15.9	11.5	5.3	17.1	0.7	3
17 hours	78.2	68.7	15.6	11.1	5.3	17.1	0.7	3.1

[0039] It can be seen that this blend of solvents, although remaining substantially azeotrope-like in behavior, changes its vapor composition quickly and dramatically. The TDCE ratio between the boil and rinse sump changes by more than 10% from the original values (67.7 weight % to 78.2 weight %).

Comparative Example 2. Distillation of Opteon SF79

Composition of Opteon SF79 over time in a vapor degreaser						
	wt. % TDCE		wt. % HFX-110		wt. % Vertrel XF	
Virgin (Drum)	95.1		4.1		0.8	
Time Distilled	Boil Sump	Rinse Sump	Boil Sump	Rinse Sump	Boil Sump	Rinse Sump
4.5 hours	95.64	95.05	4.23	4.03	0.13	0.92
13 hours	95.63	95.29	4.27	4.08	0.1	0.63
21.5 hours	95.61	95.28	4.24	4.1	0.15	0.62
29.5 hours	95.6	95.35	4.27	4.1	0.13	0.55
% change	+0.5	+0.3	+4.1	0	-83.7	-31.2

[0040] It can be seen that this product blend also sustains a significant change in the weight percentage of Vertrel XF in the blend between the “boil” and “rinse” flasks. Most dramatically, the Vertrel XF which is present to improve the non-flammable characteristic of the blend, has been substantially depleted in the boil flask early in the distillation process.

Comparative Example 3. Distillation of Opteon SF80

Composition of Opteon SF80 over time in a vapor degreaser						
	wt. % TDCE		wt. % HFX-110		wt. % SF33	
Virgin (Drum)	95.04		4.1		0.87	
Time Distilled	Boil Sump	Rinse Sump	Boil Sump	Rinse Sump	Boil Sump	Rinse Sump
1 hours	95.54	95.28	4.43	4.01	0.03	0.71
2 hours	95.54	95.15	4.40	4.03	0.03	0.82
3 hours	95.57	95.10	4.37	4.05	0.04	0.85
4 hours	95.60	95.15	4.36	4.05	0.03	0.80
% change	+0.6	+0.1	+6.3	-1.2	-96.6	-8.0

[0041] It can be seen that this product blend also changes ratio between the "boil" and "rinse" flasks. Most dramatically, the SF33 which is present to improve the non-flammable characteristic of the blend, has been substantially depleted in the boil sump.

Example 4. Blend 25-68-2, an embodiment of the present invention, was subjected to fractional distillation and the results are tabulated in Table 1 below.

Table 1

25-68-2 Fractional distillation data

Fraction	HF-7300	TDCE	EtOH	AS300	distillation Temp (°C)	head temp (°C)	% Solvent Remaining
virgin concentration	15	63	2	20			100%
1	11.96	65.06	2.91	20.07	46	45.5	91%
2	11.53	64.50	3.57	20.33	46	45.5	83%
3	12.06	66.35	2.42	19.16	47	45.7	74%
4	12.22	66.12	2.33	19.31	47	45.8	65%
5	12.46	65.89	2.18	19.44	47	45.9	55%
6	12.64	65.77	2.00	19.58	47	45.9	44%
7	12.96	65.46	1.74	19.82	47	46.1	34%
8	13.46	65.10	1.36	20.06	47	46.2	24%
9	14.05	64.66	0.93	20.33	47	44.4	14%
10	15.16	63.67	0.43	20.72	47	46.7	6%
% Component difference	-1.07	-1.06	78.50	-3.60			

Figure 2 graphically illustrates the data from Table 1.

Example 4 shows that this embodiment of the present invention maintains azeotrope-like characteristics during about 70% of a fractional distillation, before a 20% shift in concentration of the ethanol ingredient. This is within the safe operating parameters of a vapor degreasing operation.

Composition of 25- 68-2 Distillate from Fraction 5, rounded off to whole numbers.

13% HFE-7300

67% TDCE

2% EtOH

20% AS300

ASTM D56 Flash point testing for fractions 1-5 found no detectable flash. Similarly, the dual bulb distillation of solvent blend 25-68-2 is also an indicative of azeotrope type behavior of this blend as shown by the following Table 2. The blend composition is only slightly changed until Turnover 6. (The term “Turnover” refers to the number of rinse sump volumes distilled per turn.) Dual bulb distillation closely mimics efficient vapor degreasing operations.

Table 2 25-68-2 Dual bulb distillation

	Boil Sump				Rinse Sump			
Fraction	HFE-7300	TDCE	ethanol	AS300	HFE-7300	TDCE	ethanol	AS300
virgin concentration	15	63	2	20	15	63	2	20
1	14.38	64.03	1.31	20.26	11.65	65.9	2.28	20.15
2	14.3	64.09	1.33	20.26	11.76	65.89	2.22	20.11
3	14.33	64.03	1.31	20.3	11.86	65.74	2.15	20.22
4	14.4	63.96	1.18	20.43	11.88	65.79	2.14	20.16
5	14.51	63.8	1.14	20.53	11.87	65.82	2.16	20.13
6	14.53	63.82	1.16	20.48	11.94	65.73	2.13	20.19
% component difference	3.13	-1.30	42.00	-2.40	20.40	-4.33	-6.50	-0.95

Table 2 25-68-2 Dual bulb distillation (Continued)

Fraction	Turnover	Boil Temp	Vapor Temp
virgin concentration	0		
1	1	47	46.5
2	2	47	46.5
3	3	47	46.5
4	4	47	46.5
5	5	47	46.5
6	6	47	46.5
% component difference			

Figure 3 graphically illustrates the data from Table 2.

The Kb value of Example 4 is 99 and that represents good solvation and thereby efficient cleaning actions.

Example 5. Blend 25-74-1, an embodiment of the present invention, was subjected to fractional distillation as presented in Table 3. The fraction till 76% of the distillation is indicative of the azeotrope like characteristics of this solvent blend.

Table 3 25-74-1 Fractional distillation

Fraction	HFE-7300	TDCE	AS300	distillation Temp (°C)	head temp (°C)	% Solvent Remaining
virgin blend	9	75	16			100%
1	9.73	71.77	18.48	48	46.8	92%
2	9.69	72.15	18.14	48	46.8	84%
3	9.69	72.37	17.93	49	46.9	76%
4	9.70	72.55	17.73	49	46.9	68%
5	9.67	72.82	17.50	49	46.9	60%
6	9.60	73.22	17.16	49	46.9	52%
7	9.52	73.68	16.79	49	47	43%
8	9.39	74.24	16.36	49	46.9	33%
9	8.99	75.44	15.56	49	47	24%
% Component difference	0.11	-0.59	2.75			

Figure 4 graphically illustrates the data from Table 3.

The results of dual bulb fractionation of solvent blend 25-74-1 are presented in Table 4.

Table 4

	Boil			Rinse					
	HFE-7300	TDCE	AS300	HFE-7300	TDCE	AS300	Turnover	Boil Temp	Vapor Temp
virgin blend	9	75	16	9	75	16	0	100%	
1	8.32	76.56	14.7	8.32	76.56	14.7	1	48	47
2	8.25	77.09	14.65	9.63	73.71	17.08	2	48	47
3	8.24	77.08	14.67	9.59	73.4	16.99	3	48	47
4	8.17	77.21	14.6	9.6	73.44	16.95	4	48	47
5	8.14	77.27	14.58	9.55	73.55	16.89	5	48	47
6	8.08	77.4	14.5	9.53	73.63	16.83	6	49	46.9
7	8.03	77.5	14.46	9.5	73.73	16.75	7	49	47
8	7.94	77.69	14.35	9.47	73.8	16.71	8	49	47
9	7.9	77.75	14.33	9.42	73.94	16.62	9	49	46.9
% Component difference	-12	4	-10	5	-1	4			

Figure 5 graphically illustrates the data from Table 4.

Dual bulb data even after 8 turnovers remain practically unchanged (Kb of 99) also supports efficient vapor degreasing cleaning performance.

The following Examples 6 and 7 are based on medium TDCE content levels (<60 wt % TDCE). Medium TDCE levels may be needed when plastic substrate compatibilities are required, that is, if plastic surfaces of the substrates are not to be degraded.

Example 6, solvent blend 25-64-3 has the following initial amounts of components:

HFE 356: 36. wt %

TDCE 52.8 wt %

AS300 11.2 wt %

Fractional distillation of this blend yielded the following results.

Table 5

Fractional distillation of 25-64-3

Fraction	HFE-356	Trans	AS300	distillation Temp (°C)	head temp (°C)	% Solvent Remaining
virgin blend	36	52.8	11.2			100%
1	36.38	52.60	11.02	45	43.2	92%
2	40.58	54.25	14.65	45	43.6	85%
3	40.08	51.67	8.23	45	43.6	76%
4	39.74	51.69	8.55	45	43.7	68%
5	39.31	51.80	8.87	45	43.9	60%
6	38.70	51.99	9.29	45	43.9	52%
7	38.17	52.09	9.72	45	43.9	44%
8	37.37	52.25	10.36	45	44	35%
9	36.05	52.67	11.27	45	44	27%
10	34.32	53.15	12.51	45	44.2	18%
% Component difference	-4.67	0.66	11.70			

At 80% of the distillation, less than 20% variation in the component ratios is a clear indication of an azeotrope like blend.

Figure 6 graphically illustrates the data from Table 5.

The dual bulb distillation of solvent blend 25-64-3 shows, even at Turnover 8, only a small variation in component ratios, demonstrating that this blend is an azeotrope-like solvent.

Table 6

The Dual bulb distillation of 25-64-3

	Boil			Rinse					
	HFE-356	TDCE	AS300	HFE-356	TDCE	AS300	Turnover	Boil Temp	Vapor Temp
virgin blend	36	52.8	11.2	36	52.8	11.2	0		
1	32.08	53.95	13.96	38.63	52.02	9.34	1	44	42.7
2	31.4	54.22	14.36	37.88	52.2	9.9	2	44	42.9
3	31.53	54.18	14.28	37.68	52.25	10.06	3	44	42.9
4	31.43	54.25	14.34	37.54	52.29	10.16	4	44	42.9
5	31.19	54.3	14.5	37.35	52.37	10.27	5	45	42.9
6	31.05	54.38	14.56	37.19	52.38	10.42	6	45	42.9
7	30.94	54.4	14.65	37.03	52.46	10.51	7	44	42.9
8	30.73	54.42	14.83	36.86	52.53	10.6	8	45	43
9	30.15	54.68	15.17	36.7	52.55	10.75	9	45	43
% Component difference	-16.25	3.56	35.45	1.94	-0.47	-4.02			

Figure 7 graphically illustrates the data from Table 6.

The solvent blend of Example 6 has a KB value of 57 and tested non-flammable.

Example 7 Fractional distillation of formula 25-65-1

In this formulation there are two low boiling HFE solvent component. HFE 356 and AE3000 (1,1,2,2 tetrafluoroethyl 2,2,2-triethyl ether), each has a boiling point of about 54°C.

Table 7

Fraction	HFE356	AE3000	TDCE	Ethanol	distillation Temp (°C)	head temp (°C)	% Solvent Remaining
virgin blend	20	26.5	50.5	3			100%
1	19.61	27.87	49.55	2.95	43	41.4	93%
2	18.66	29.62	49.30	2.4	43	41.5	85%
3	18.85	29.39	49.29	2.45	43	41.9	77%
4	19.04	29.15	49.28	2.51	43	41.8	69%
5	19.22	28.93	49.29	2.54	43	41.9	61%
6	19.43	28.62	49.33	2.59	43	41.9	53%
7	19.67	28.29	49.37	2.65	43	41.9	46%
8	19.88	27.96	49.44	2.71	43	42	38%
9	20.18	27.53	49.49	2.78	43	42.2	30%
10	20.53	26.94	49.62	2.89	43	42.2	23%
% Component difference	5.10	-2.30	-1.05	3.67			

Figure 8 graphically illustrates the data from Table 7.

Table 8

Table 8 shows the results of dual bulb distillation of blend 25-65-1

	Boil				Rinse			
	HFE-356	AE3000	TDCE	ethanol	HFE-356	AE3000	TDCE	ethanol
virgin blend	20.0	26.5	50.5	3.0	20.0	26.5	50.5	3.0
1	20.23	26.37	49.8	3.6	19.24	28.72	49.44	2.58
2	20.33	26.14	49.8	3.73	19.41	28.52	49.45	2.62
3	20.3	26.19	49.76	3.75	19.43	28.43	49.51	2.63
4	20.3	26.19	49.75	3.76	19.46	28.4	49.5	2.64
5	20.31	26.12	49.74	3.83	19.48	28.36	49.51	2.65
6	20.32	26.08	49.7	3.9	19.54	28.37	49.42	2.67
7	20.32	26.06	49.66	3.96	19.55	28.26	49.51	2.68
8	20.33	25.98	49.63	4.06	19.61	28.24	49.41	2.74
9	20.35	25.94	49.52	4.19	19.63	28.22	49.42	2.73
% component difference	1.75	-2.11	-1.94	39.67	-1.85	6.49	-2.14	-9.00

Table 8 (Continued)

Table 8 shows the results of dual bulb distillation of blend 25-65-1

		Boil	Vapor
	Turnover	Temp	Temp
virgin blend			
1	1	43	42.1
2	2	43	42
3	3	43	41.9
4	4	42	41.9
5	5	43	42
6	6	43	42
7	7	43	42
8	8	43	41.9
9	9	43	41.9
% component difference			

Blend 25-65-1 has a Kb value of 58 and tested nonflammable.

Figure 9 graphically illustrates the data from Table 8.

Example 8 Fractional Distillation of 18-119-5

Table 9

Table 9 Fractional distillation of this embodiment consists of a high-concentration blend of trans-dichloroethylene (TDCE) with a high-boiling HFE and a HFCO.

Fraction	7300%	TDCE%	AS300%	Bottom Temp (°C)	Top Temp (°C)	% Solvent Remaining
0	4.98	90.07	4.95	47.7	51	100%
1	9.09	84.06	6.85	47.70	52	91%
2	7.96	85.64	6.40	47.9	52	82%
3	6.84	87.22	5.94	48.00	52	74%
4	6.72	87.40	5.88	48.00	52	65%
5	6.11	88.25	5.64	48.00	52	56%
6	4.60	90.39	5.01	48.10	52	48%
7	4.11	91.11	4.78	48.20	52	39%
8	2.40	93.73	3.87	48.50	52	29%
9	1.65	95.02	3.33	48.60	52	21%
10	0.68	96.91	2.41	487.70	52	14%

Table 10

Table 10 demonstrates the dual bulb distillation of blend 18-119-5.

Sample	Boil			Rinse		
	7300%	TDCE%	AS300%	7300%	TDCE%	AS300%
0	4.82	90.33	4.85	4.82	90.33	4.85
1	2.72	93.53	3.75	7.16	86.82	6.02
2	2.52	93.89	3.59	6.57	87.64	5.79
3	2.70	93.65	3.65	6.26	88.09	5.65
4	2.63	93.77	3.61	6.16	88.29	5.60
5	2.73	93.62	3.66	6.03	88.44	5.53
6	2.65	93.75	3.60	5.40	88.58	5.49
7	2.61	93.81	3.58	5.85	88.71	5.44
8	3.61	92.24	4.16	5.80	88.79	5.41

Figure 10 graphically illustrates the data from Table 10.

Blend 18-119-5 is nonflammable and has a KB value of 115.

Table 11 demonstrates blend 25-68-2 in a vapor degreaser over a series of 4 days.

	Boil			
	tDCE	AS300	HFE-7300	ethanol
initial make up	62.90	20.06	14.89	2.06
Day 1	62.34	22.20	14.50	0.95
Day 2	61.51	21.89	15.60	0.96
Day 3	61.34	21.90	15.80	0.96
Day 4	61.03	21.94	16.09	0.94

Table 11 (Continued)

	Rinse			
	tDCE	AS300	HFE-7300	ethanol
initial make up	62.90	20.06	14.89	2.06
Day 1	63.98	21.10	13.09	1.83
Day 2	64.58	21.61	12.08	1.74
Day 3	64.54	21.66	12.09	1.71
Day 4	64.50	21.68	12.11	1.71

Figure 11 graphically illustrates the data from Table 11.

[0042] While the present invention has been described in detail with reference to specific embodiments thereof, these embodiments are exemplary and not limiting.

THE CLAIMS

What is claimed is:

1. A solvent composition comprising from about 40 wt % to about 90 wt % trans-dichloroethylene, a monochlorotrifluoropropene, a hydrofluoroether and, optionally, a C1 to C3 alcohol.

2. The solvent composition of claim 1 wherein the monochlorotrifluoropropene is selected from the group consisting of one or more of transCF₃CH=CClH (1233zdZ); cisCF₃CH=CClH (1233zdZ); transCHF₂CF=CClH (1233ydE); cisCHF₂CF=CClH (1233ydZ); transCHF₂CH=CClF (1233zbE); cisCHF₂CH=CClF (1233zbZ); transCHF₂CCl=CHF (1233xeE); cisCHF₂CCl=CHF (1233xeZ); CH₂FCCl=CF₂ (1233x0); transCHFC1CF=CFH (1233yeE); cisCHFC1CF=CFH (1233yeZ); CH₂C1CF=CF₂ (1233yc); CF₂C1CF=CH₂ (1233xf).

3. The solvent composition of claim 1 wherein the hydrofluoroether is selected from the group consisting of one or more of ethoxynonafluorobutane, 1,1,2,3,3,3-hexafluoropropyl-2,2,2-trifluoroethyl ether, 1,1,2,2-tetrafluoroethyl-2,2,3,3,3-pentafluoropropyl ether, 1,1-difluoroethyl-2,2,3,3-tetrafluoropropyl ether, 1,1,2,3,3,3-hexafluoropropyl-2,2,3,3,3-pentafluoropropyl ether, 1,1,2,2-tetrafluoroethyl-2,2,3,3,3-tetrafluoropropyl ether, 1,1,2,3,3,3-hexafluoropropyl-2,2,3,3-tetrafluoropropyl ether, and 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane.

4. The solvent composition of claim 2 wherein the hydrofluoroether is selected from the group consisting of one or more of ethoxynonafluorobutane, 1,1,2,3,3,3-hexafluoropropyl-2,2,2-trifluoroethyl ether, 1,1,2,2-tetrafluoroethyl-2,2,3,3,3-pentafluoropropyl ether, 1,1-difluoroethyl-2,2,3,3-tetrafluoropropyl ether, 1,1,2,3,3,3-hexafluoropropyl-2,2,3,3,3-pentafluoropropyl ether, 1,1,2,2-tetrafluoroethyl-2,2,3,3,3-tetrafluoropropyl ether, 1,1,2,3,3,3-hexafluoropropyl-2,2,3,3-tetrafluoropropyl ether, and 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane.

5. The solvent composition of claim 1 comprising from about 59 to about 70 wt % trans-dichloroethylene (TDCE), from about 10 to about 25 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300), from about 11 to about 18 wt % 3-methoxy-4-trifluoromethyl-

1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300) and from about 1 to about 5 wt% ethanol.

6. The solvent composition of claim 1 comprising from about 70 to about 80 wt % trans-dichloroethylene (TDCE), from about 11 to about 21 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and from about 5 to about 15 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300).

7. The solvent composition of claim 1 comprising from about 40 to about 60 wt % trans-dichloroethylene (TDCE), from about 11 to about 21 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and from about 20 to about 40 wt % 1,1,1,2,3,3-hexafluoro-3-methoxy propane (HFE-356).

8. The solvent composition of claim 1 comprising from about 40 to about 60 wt % trans-dichloroethylene (TDCE), from about 15 to about 40 wt % of 1,1,2,2 tetrafluoroethyl 2,2,2-triethyl ether (AE3000) and from about 10 to about 25 wt % 1,1,1,2,3,3-hexafluoro-3-methoxy propane (HFE-356).

9. The solvent composition of claim 3 further comprising a surfactant in a concentration of from about 0.1 to about 3 wt %.

10. The solvent composition of claim 3 further comprising a cosolvent in an amount of from about 1 to about 50 wt % of all the other ingredients of the solvent composition.

11. A solvent composition exhibiting azeotrope-like properties and comprising from about 71 to about 75 wt % trans-dichloroethylene (TDCE), from about 15 to about 19 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and from about 7 to about 10 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300).

12. The composition of claim 11 comprising from about 85 to about 95 wt % trans-dichloroethylene (TDCE), from about 1 to about 5 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and from about 1 to about 5 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300).

13. The composition of claim 11 comprising about 90 wt % trans-dichloroethylene (TDCE), about 5 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and about 5 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300).

14. The composition of claim 11 comprising from about 59 to about 70 wt % trans-dichloroethylene (TDCE), from about 10 to about 25 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300), from about 11 to about 18 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300) and from about 1 to about 5 wt % ethanol.

15. The composition of claim 11 comprising about 63 wt % trans-dichloroethylene (TDCE), about 20 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300), about 15 wt % 3-methoxy-4-trifluoromethyl-1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFE-7300) and about 2 wt % ethanol.

16. A solvent composition exhibiting azeotrope-like properties and comprising from about 40 to about 60 wt % trans-dichloroethylene (TDCE), from about 15 to about 40 wt % of 1,1,2,2 tetrafluoroethyl 2,2,2-triethyl ether (AE3000) and from about 10 to about 25 wt % 1,1,1,2,3,3-hexafluoro-3-methoxy propane (HFE-356).

17. The composition of claim 16 comprising from about 40 to about 60 wt % trans-dichloroethylene (TDCE), from about 11 to about 21 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and from about 20 to about 40 wt % 1,1,1,2,3,3-hexafluoro-3-methoxy propane (HFE-356).

18. The composition of claim 16 comprising about 53 wt % trans-dichloroethylene (TDCE), about 11 wt % of 1-chloro-2,3,3-trifluoro-1-propene (AS300) and about 36 wt % 1,1,1,2,3,3-hexafluoro-3-methoxy propane (HFE-356).

19. A method for cleaning soiling substances from metal, ceramic and synthetic polymer articles comprising contacting one or more of the articles with the solvent composition of any of claims 3, 10, 11, 12, 13, 14, 15, 16, 17 or 18, and removing the composition from the one or more articles.