

ORGANIC-BASED COMPOSITIONField of the Invention

This invention relates to an organic-based composition. More particularly, this invention relates to a composition which is particularly suitable for use in removing contaminants such as oils, particulates, and other soils from substrates and which has other uses, as described below.

Presently in the cleaning industry, there is a movement to use cleaning compositions with favorable environmental properties, including low ozone depletion potential and low global warming potential. Traditionally, the industry has relied heavily on the use of cleaning compositions which are considered now as having unfavorable environmental properties. Examples of such cleaning compositions are those which contain chlorinated hydrocarbons. The use of chlorinated hydrocarbons presents a threat to the environment because such materials are involved in stratospheric ozone depletion. Therefore, alternative cleaning compositions that do not contain chlorinated hydrocarbon solvents are environmentally attractive.

Desirable cleaning compositions, in addition to being environmentally attractive, should also be safe to the user. Accordingly, they should be nonflammable under the conditions of use and be non-toxic or at the least have very low toxicity.

For maximum effectiveness, a cleaning composition, in addition to being an effective cleaner, must have a combination of desired properties, including being non-ozone-

depleting, non-toxic, nonflammable, fast drying, and compatible with the articles being cleaned.

Cleaning compositions can be classified broadly as inorganic-based, for example, water-based, and organic-based, for example, hydrocarbon solvent based. The present invention relates to the latter type of cleaning composition, that is, an organic-based composition.

Reported Developments

There have been developed a myriad of cleaning compositions which do not require the use of chlorinated hydrocarbons. A summary of various of these compositions follows.

U.S. Patent No. 5,531,916 to Merchant discloses a cleaning composition comprising an acyclic aliphatic hydrofluorocarbon and a co-solvent selected from alcohols, esters, ethers, ketones, acetonitrile, and nitromethane. Some of the disclosed compositions are azeotropic.

U.S. Patent No. 5,395,548 to Pfahl, Jr. et al. discloses a cleaning composition comprising a low to moderate boiling point, fluorinated or non-fluorinated alcohol and a relatively non-volatile, higher boiling point organic liquid from the terpene family or a high boiling point aprotic solvent. The composition is non-azeotropic, such that, when it is heated, a vapor formed of the alcohol overlies the underlying higher boiling point liquid.

U.S. Patent Nos. 5,221,493; 5,176,757; 5,073,290; and 5,073,288 disclose cleaning compositions comprising specified fluorinated compounds mixed with one or more of alcohols, ethers, esters, ketones, and nitrogen-containing organic compounds. The compositions are azeotropic.

U.S. Patent No. 5,143,652 to Slinn discloses a cleaning composition comprising a perfluorocarbon, isopropanol and water. U.S. Patent No. 5,055,138 to Slinn discloses a cleaning composition comprising a highly fluorinated organic compound (HFO) and a hydrogen-containing flammable liquid organic solvent. The two components are mostly immiscible. In use, the composition is heated to the boiling point of the HFO. This results in the formation of a nonflammable HFO vapor layer which covers the underlying flammable organic

solvent and thereby reduces the fire hazard associated with the flammable solvent.

U.S. Patent No. 4,828,751 to Kremer discloses a composition for cleaning silicon wafers, the composition consisting essentially of a haloalkylhydrocarbon and a partially fluorinated alcohol. U.S. Patent No. 4,169,807 to Zuber discloses a composition for drying silicon wafers, the composition comprising a perfluorocyclic compound, 1-propanol, and water.

U.S. Patent No. 4,276,186 to Bakos et al. discloses a cleaning composition comprising at least about 50% by weight of N-methyl-2-pyrrolidone and at least about 10% by weight of a water miscible alkanolamine. The cleaning composition can contain up to about 35% of other solvents, including for example, aromatic hydrocarbons, cycloaliphatics, ketones, and fluorinated hydrocarbons.

There are one or more disadvantages associated with use of the above compositions, including, for example, flammability hazards, toxicity, non-compatibility with sensitive substrates, and limited flexibility with regard to the types of soils removed from contaminated substrates. The present invention provides a cleaning composition which is nonflammable, non-toxic, compatible with sensitive materials such as plastics and which has the capability of cleaning effectively a wide variety of contaminants from the surfaces of articles without degrading or otherwise affecting adversely the material comprising the surface of the article. The composition of the present invention is useful also as a carrier for one or more other materials which can be deposited on the surface of an article, for example, in the form of a film.

Summary of the Invention

In accordance with the present invention, there is provided an azeotropic nonflammable liquid composition which has cleaning properties, which has an ozone depletion factor of no greater than about 0.15, and which comprises the following volatile constituents, each of which has an ozone depletion factor of no greater than about 0.15: (a) a liquid nonflammable fluorinated compound; (b) a low polarity solvent

which is capable of dissolving no greater than about 10% water by volume, preferably no greater than about 0.1%; and (c) a high polarity solvent which is capable of dissolving at least about 10% water by volume. The cleaning composition is substantially free of chlorinated hydrocarbon solvents and preferably contains no chlorinated hydrocarbon solvents.

The cleaning composition should be compatible with the substrate on which it is to be used. That is, the composition should not attack or damage the substrate under the conditions of use.

In preferred form, the fluorinated compound is selected from the group consisting of fluorocarbons, hydrofluorocarbons, fluoroethers, and hydrofluoroethers, the low polarity solvent is selected from the group consisting of n-propyl bromide, terpenes, polymethylsiloxanes, and petroleum solvents, and the high polarity solvent is selected from the group consisting of low molecular weight alcohols and low molecular weight glycol ethers.

In preferred form, the cleaning composition has an ozone depletion factor of about 0 and comprises: (a) from about 50 wt.% to about 80 wt.% of the fluorinated compound; (b) from about 15 wt.% to about 40 wt.% of the liquid low polarity solvent; and (c) from about 3 wt.% to about 12 wt.% of the liquid high polarity solvent.

Another aspect of the present invention comprises a process for removing adherent soils from a soiled substrate comprising: (a) contacting the soiled substrate with an azeotropic nonflammable liquid cleaning composition which is compatible with the substrate for a time sufficient to remove the adherent soils, the cleaning composition having an ozone depletion factor of no greater than about 0.15, and comprising the following constituents, each having an ozone depletion factor of no greater than about 0.15: (i) a liquid nonflammable fluorinated compound; (ii) a liquid low polarity solvent which is capable of dissolving no greater than about 10% water by volume, preferably less than about 0.1%; and (iii) a liquid high polarity solvent which is capable of dissolving at least about 10% water by volume; and (b) removing the substrate from the liquid cleaning composition.

Preferably, the cleaning composition contains no chlorinated hydrocarbon solvents.

The cleaning method of the present invention may be performed at room temperature or at elevated temperature.

5 Still another aspect of the present invention comprises:
(A) heating the liquid cleaning composition to its boiling point to form a vapor phase which overlies the boiling liquid cleaning composition, the vapor phase comprising the
10 nonflammable fluorinated compound, the low polarity solvent, and the high polarity solvent, each present in the same proportion as present in the boiling liquid composition; (B) contacting the soiled substrate with the boiling cleaning composition; (C) withdrawing the substrate from the boiling cleaning composition and into the vapor phase; (D) contacting
15 the substrate with the vapor phase; and (E) withdrawing the substrate from the vapor phase.

The present invention has a number of advantages associated with its use. The present cleaning composition is environmentally attractive in that it is effective in the
20 absence of the use of compounds which contain chlorinated hydrocarbon solvents or other materials which possess high ozone-depletion and/or high global warming potential. Additionally, the cleaning composition includes embodiments which are particularly suitable for use in cleaning sensitive
25 plastics and elastomers, which are attacked by other cleaning compositions. Furthermore, there is no flammability hazard associated with the cleaning composition as it is nonflammable under the conditions of use.

30 A further aspect of the present invention comprises a composition which, in addition to the volatile constituents described above, includes also a non-volatile material which is dissolved in the composition and which has certain desired functional properties. Such composition can be used in a method for depositing a non-volatile functional material on a
35 surface comprising applying to the surface said composition, forming on said surface a deposit which includes said material and which is free of said fluorinated compound, the low polarity solvent, and the high polarity solvent by

effecting evaporation of the fluorinated compound, the low polarity solvent, and the high polarity solvent.

Detailed Description of the Invention

5 The cleaning composition of the present invention is azeotropic and nonflammable, has an ozone depletion factor of no greater than about 0.15, and is comprised of the following constituents: (a) a liquid nonflammable fluorinated compound; (b) a low polarity solvent; and (c) a high polarity solvent. Each of the components comprising the composition
10 has an ozone depletion factor of no greater than about 0.15, preferably about 0.

An important feature of the present invention is that it is azeotropic. An azeotropic composition is a liquid mixture which includes two or more substances that behave like a
15 single substance in that the vapor produced by partial evaporation or distillation of the composition has the same composition as that of the liquid. An azeotropic composition boils at a constant temperature and distills without a substantial change in composition. The constituents
20 comprising the composition are present in amounts such that the composition is azeotropic.

The boiling point of an azeotropic composition is generally lower than the boiling point of each of the individual constituents of the composition. It is believed
25 that, for most embodiments of the composition of the present invention, the boiling point will be within the range of from about 120°F (49°C) to about 140°F (60°C). It should be understood, however, that compositions having boiling points outside of this range can be formulated. Preferred
30 embodiments have a boiling point in the range of from about 125°F (52°C) to about 135°F (57°C).

Because an azeotropic composition has a constant boiling point, constituents of the azeotropic composition evaporate at essentially the same rate. The constituents of the
35 present azeotropic composition have essentially the same evaporation rate at use conditions, resulting in no preferential evaporation of any one constituent over another.

Another important property of the composition of the present invention is that it is nonflammable. By nonflam-

mable, it is meant that the present composition has no flash point. The fluorinated compound constituent is nonflammable in that it has no flash point. Although various of the other constituents of the composition may have flash points, when each of the nonflammable fluorinated compound, the low polarity solvent, and the high polarity solvent constituents are mixed together to form the composition of the present invention, the resulting composition has no flash point and is, therefore, nonflammable.

As mentioned above, the vapor produced by partial evaporation or distillation of the composition has substantially the same composition as the liquid. The nonflammable fluorinated compound, the low polarity solvent, and the high polarity solvent are thus each present in the same proportion in the vapor as they are in the liquid composition. The fluorinated compound is present in the cleaning composition (in both the liquid and vapor phase) in a major amount, that is, in an amount greater than each of the other constituents.

The cleaning composition of the present invention also has little or no known tendency to cause depletion of the ozone layer. Accordingly, the cleaning composition has an ozone depletion factor of no greater than about 0.15, preferably no greater than about 0.05, and more preferably about 0. Ozone depletion factors are reported in Technical Progress on Protecting the Ozone Layer - Electronics, Degreasing and dry Cleaning Solvents Technical Options report, United Nations Environment Programme (6/30/89).

It is preferred that the cleaning composition of the present invention be substantially free of water. This means that the cleaning composition contains preferably no greater than about five percent by weight of water. More preferably, the composition contains no more than about one percent by weight of water. A water-free cleaning composition is especially preferred. While aqueous systems have certain desirable characteristics, such as ready availability and low costs, cleaning compositions containing water are corrosive to many types of materials that need to be cleaned.

Additionally, substrates which are cleaned with water-containing systems are difficult to dry.

The nonflammable fluorinated compound functions to render the cleaning composition compatible with sensitive elastomers and other plastics. It has good compatibility with such materials. Accordingly, the fluorinated compound can be used to alter the compatibility of the composition so that it is compatible with sensitive materials, including, for example, plastics. The fluorinated compound generally has poor solvency for most soils and water.

The fluorinated compound of the present invention has little or no known tendency to cause depletion of the ozone layer. It is preferred that the fluorinated compound have an ozone depletion factor of no greater than about 0.05, and more preferably of about 0.

The fluorinated compound is a liquid at room temperature and may either be perfluorinated or partially fluorinated. By perfluorinated, it is meant that all the hydrogen atoms attached to the carbon atoms in the backbone of the fluorinated compound have been replaced by fluorine. In a partially fluorinated compound, there is at least one hydrogen atom attached to a carbon atom in the backbone of the fluorinated compound. The fluorinated compound may also contain other elements, for example, oxygen and/or nitrogen atoms. Typically, the fluorinated compound will contain from 1 to about 15 carbon atoms. It is preferred to use a fluorinated compound having from 4 to about 10 carbon atoms.

The fluorinated compound of the present invention is preferably selected from the group consisting of fluorocarbons, hydrofluorocarbons, fluoroethers, and hydrofluoroethers. Examples of such compounds include methyl nonafluorobutyl ether, methyl nonafluoroisobutyl ether, 1,1,1,2,3,4,4,5,5,5-decafluoropentane, perfluorohexane, and perfluoroheptane. Preferred embodiments of the present composition contain partially fluorinated compounds. Particularly preferred embodiments include hydrofluoroethers. Especially preferred fluorinated compounds are nonafluorobutyl ether and a mixture of methyl nonafluorobutyl ether and methyl nonafluoroisobutyl ether.

As mentioned above, the fluorinated compound is present in the composition in an amount greater than the amount of any of the other constituents. In preferred embodiments, the fluorinated compound comprises from about 50 wt.% to about 80 wt.%, and more preferably from about 55 wt.% to about 75 wt.% of the composition.

Another constituent of the present cleaning composition is a low polarity solvent. This constituent functions to dissolves oils and hydrocarbon residues and other organic-based residues. The low polarity solvent has little solvency for water and water-like materials and is capable of dissolving no greater than about 10% water by volume.

The low polarity solvent of the present invention has little or no known tendency to cause depletion of the ozone layer. It is preferred that the low polarity solvent compounds have an ozone depletion factor of no greater than about 0.05, and even more preferably of about 0.

The low polarity solvent of the present composition is preferably selected from the group consisting of n-propyl bromide, terpenes, polymethylsiloxanes, petroleum solvents, and aliphatic esters, including, for example, monobasic esters and diesters. Preferred embodiments include n-propyl bromide and polymethylsiloxanes. An especially preferred polymethylsiloxane is octamethyltrisiloxane. Various of the preferred low polarity solvents have nominal solvency for water. For example, the literature reports that terpenes are capable of dissolving less than 0.1% by volume of water and that n-propyl bromide and polymethylsiloxanes dissolve even smaller amounts of water. It is preferred that the low polarity solvent be a material which is capable of dissolving no greater than about 0.1 % by volume of water.

The low polarity solvent should be present in the composition in an amount which is effective to accomplish its cleaning function. This can be accomplished by including in the composition a minor amount of the low polarity solvent. Preferably the low polarity solvent comprises from about 15 wt.% to about 40 wt.% of the composition.

Another constituent of the present cleaning composition is a high polarity solvent. This constituent functions to

dissolve a variety of soils, for example, ionic residues, including fingerprints, particulate residues, water-soluble oils and other water-soluble soils. The high polarity solvent has good solvency for water and water-like materials and is capable of dissolving at least about 10% water by volume.

The high polarity solvent of the present invention has little or no known tendency to cause depletion of the ozone layer. It is preferred that the high polarity solvent have an ozone depletion factor of no greater than about 0.05 and even more preferably of about 0.

Examples of high polarity solvents are alcohols, ethers, and ketones. The high polarity solvent of the present composition is preferably selected from the group consisting of low molecular weight alcohols (1 to about 10 carbon atoms) and low molecular weight glycol ethers. Preferred low molecular weight alcohols are those having from 1 to about 5 carbon atoms. Preferred embodiments include methanol, ethanol, and n-propanol. An especially preferred low molecular weight alcohol is isopropanol. Preferred low molecular weight glycol ethers include propylene glycol ethers.

The high polarity solvent should be present in the composition in an amount which is effective to accomplish its cleaning function. This can be accomplished by including in the composition a minor amount of the high polarity solvent. Preferably, the high polarity solvent comprises from about 3 wt.% to about 12 wt.% of the composition.

As mentioned above, the composition is substantially free of chlorinated hydrocarbon solvents, that is, amounts less than about 5 wt.%. Preferably, the composition contains less than 1 wt.% of chlorinated hydrocarbon solvent, and most preferably, it contains none of such material.

The nonflammable fluorinated compound, low polarity solvent, and high polarity solvent constituents of the cleaning composition of the present invention are preferably miscible with each other. The term "miscible" is used herein in its usual sense to mean that the liquid fluorinated compound, the liquid low polarity solvent, and the liquid

high polarity solvent mix with each other to form a uniform blend, that is, to dissolve in each other. Thus, a composition of this embodiment of the invention preferably comprises one uniform liquid phase.

5 Another important aspect of the present invention is that embodiments of the cleaning composition are compatible with a wide variety of substrates to be cleaned, including, for example, sensitive plastics and other materials which tend to be degraded by conventional solvents. Degradation is
10 evidenced by swelling, discoloration, crazing and cracking. Embodiments of the composition are non-damaging to a wide range of materials, including metallic surfaces and plastic surfaces, for example, polycarbonates, acrylics, and acrylonitrile-butadiene-styrene terpolymer (ABS).

15 The term "plastic-compatible" is used herein to refer to embodiments of the composition of the present invention which do not degrade various types substrates that are cleaned with the composition. A composition is "plastic-compatible" when it passes the following test. A clean polycarbonate specimen
20 about $1\frac{1}{2}$ " x $1\frac{1}{2}$ " and having a thickness of 3.15 mm is weighed on an analytical balance and the weight of the specimen is recorded. The specimen is then placed in the cleaning composition at room temperature for 10 minutes, removed therefrom, and dried. The weight of the specimen is
25 remeasured and recorded after the weight has stabilized. Another polycarbonate specimen is treated in the same way, but placed in a boiling form of the cleaning composition. The cleaning composition is plastic-compatible when the weight changes of the specimens, if any, are no greater than
30 about 1 wt.%, when the test specimens show no signs of crazing, and there are no other visible changes in the appearance of the specimens.

35 Examples of articles that can be cleaned effectively by utilizing the cleaning composition of the present invention include medical devices, circuit boards, painted articles, costume materials, live electrical circuits, aerospace/aircraft components, articles covered with fabric, vinyl, or leather, carpets, stainless steel appliances,

polycarbonate and polyacrylic windows, and also multiply articles that are together by adhesives.

Cleaning compositions within the scope of the present invention can be used to clean effectively from the substrates a wide variety of soils. The term "soil" is used herein to include unwanted organic or inorganic materials that may be present on the substrate to be cleaned, including, for example, fingerprints, mineral oils, machining oils, silicone oils and other lubricants, rosin solder flux, hydraulic fluid, grease, waxes, particulate, and other manufacturing soils.

The soiled substrate is contacted with the cleaning composition for a time sufficient to remove the adherent soil, for example, about 30 seconds to about 10 minutes, depending on the nature of the soils and the manner of contacting the composition with the article to be cleaned.

Many techniques are known and are available to those skilled in the art for carrying out the contacting step of the present invention. The use of any suitable technique can be used in the practice of the present invention. For example, the article can be immersed in the composition or sprayed with the composition. In use, the liquid cleaning composition can be at room temperature or at elevated temperature and cleaning can be accomplished at atmospheric pressure. Ultrasonic agitation may be used to help loosen the adherent soils from the contaminated substrates.

In use, the cleaning composition may be heated to its boiling point. As mentioned above, the azeotropic cleaning composition has a single boiling point. As mentioned above also, it is believed that the most widely used compositions will have a boiling point in the range of about 120°F (49°C) to about 140°F (60°C), but it should be understood that compositions within the scope of the present invention having boiling points outside of this range can be formulated. Heating the azeotropic cleaning composition to its boiling point results in the creation of a vapor phase which overlies the boiling liquid cleaning composition. The vapor in this phase comprises the nonflammable fluorinated compound, the low polarity solvent, and the high polarity solvent, each

present in the same proportion as present in the boiling liquid composition. The vapor is non-combustible as a result of the presence of the nonflammable fluorinated compound which, as mentioned above, is present in a major amount relative to the other constituents, which may themselves be flammable.

For embodiments of the invention in which the cleaning composition is heated to its boiling point, the process involves the following steps: heating the liquid cleaning composition to its boiling point to form a vapor phase as described above, contacting the soiled substrate with the vapor phase and then with the boiling cleaning composition, withdrawing the substrate from the boiling cleaning composition and into the vapor phase, contacting the substrate with the vapor phase, and withdrawing the substrate from the vapor phase. In preferred form, the cleaning system includes not only a container in which the cleaning composition is heated to its boiling point, but also another container (or sump) which is unheated and which contains condensed cleaning composition from the vapor, including vapor which overlies the unheated container. In such system, the major cleaning is effected in the boiling composition and in the vapor, with additional cleaning being effected in the condensed cleaning composition which is clean relative to the boiling composition, the latter containing substantially higher amounts of "removed" soil than the former.

As mentioned above, another aspect of the present development comprises a composition of the aforementioned type that includes also a non-volatile functional material. The term "functional" means that the material exhibits a useful property when it is present on the surface of a substrate. For example, the material may exhibit lubricating properties or form on the surface a hard or rubbery polymeric coating that has, for example, protective properties. The functional material may be a liquid or a solid at room temperature and is soluble (or miscible) in the composition. The functional material is non-volatile in that the material does not evaporate (if a liquid) or volatilize (if a solid) as the other constituents of the composition evaporate,

leaving behind on the surface of the substrate the non-volatile material in either liquid or solid form and essentially free of the volatile constituents, that is, the nonflammable fluorinated compound, the low polarity solvent, and the high polarity solvent.

Typically, the non-volatile material will have a vapor pressure of no greater than about 0.005 millimeter of mercury (mm Hg) at 20°C. Examples of non-volatile functional materials that can be used in the practice of the present invention include silicon-containing liquids such as polydimethylsiloxanes, amino functional silicones such as dimethoxysilyldimethylaminoethylaminopropyl silicone, clyclomethicone, dimethylpolysiloxane, organofunctional dimethylpolysiloxane, dimethicone copolyol, silanol, and silicone resins, polymeric adhesives and coating materials such as, for example, acrylate esters, and fluorocarbon and petroleum-based lubricants.

The amount of non-volatile functional material included in the composition will vary depending on the nature of the material and the use to be made thereof. It is believed that, for most applications, an amount within the range of about 1 to about 10 wt.% of the functional material will be sufficient.

In practice, the composition containing the non-volatile functional solvent is applied to the surface of an article. The volatile constituents evaporate, for example, within about 1 to about 10 minutes, or longer, leaving behind the functional material, for example, in the form of a thin liquid or solid coating.

An example of an application for use of this embodiment of the present invention includes the application of a silicone oil lubricant onto the surface of a medical device such as syringe needles, catheters, and surgical tools. Other examples include application of a polymeric silicone coating to a medical device, deposition of a conformal coating onto a printed circuit assembly, and deposition of an adhesive onto a metal or plastic substrate.

As mentioned above, other constituents of the composition of the present invention are volatile in that

they are capable of evaporating at room temperature. Their vapor pressures are higher than the vapor pressure of the non-volatile functional material, indeed, typically substantially higher than the vapor pressure of the functional material. For example, the vapor pressures of herein exemplified volatile compounds range from about 4 to about 195 mm Hg at 20°C. However, it should be understood that a compound having a vapor pressure outside of this range can be used as the volatile constituent of the composition, for example, a compound having a vapor pressure within the range of from about 0.01 to less than 760 mm Hg at 20°C.

Examples

The following examples are illustrative and/or comparative, but not limiting of, the present invention. These examples provide methods of determining whether cleaning compositions are compatible with particular substrates. The designation of examples as comparative is not necessarily an indication that the examples represent prior art products or procedures.

Example 1

A preferred embodiment of the cleaning composition of the present invention is described below in Table 1.

Table 1

Component	Weight %
3M HFE 7100	75
n-propyl bromide	20
isopropyl alcohol	5

HFE 7100 is a product of 3M and is a nonflammable hydrofluoroether which includes from 20-80% of methyl nonafluorobutyl ether and from 20-80% of methyl nonafluoroisobutyl ether. About 70 parts by weight of HFE 7100, about 25 parts by weight of a low polarity solvent consisting of n-propyl bromide, and about 5 parts by weight of a high polarity solvent consisting of isopropyl alcohol were combined in a vessel at room temperature to form a liquid cleaning composition according to the present invention.

Example 2

Another preferred embodiment of the cleaning composition of the present invention is described below in Table 2.

Table 2

Component	Weight %
3M HFE 7100	54
octamethyltrisiloxane (Dow Corning OS 20)	36
isopropyl alcohol	10

About 54 parts by weight of HFE 7100, about 36 parts by weight of a low polarity solvent consisting of octamethyltrisiloxane, and about 10 parts by weight of a high polarity solvent consisting of isopropyl alcohol were combined in a vessel at room temperature to form a liquid cleaning composition according to the present invention.

Examples C-1 and C-2 below are illustrative of comparative cleaning compositions which are used in the cleaning evaluations discussed below.

Example C-1

The comparative cleaning composition of Example C-1 is described below in Table 3.

Table 3

Component	Weight %
3M HFE 7100	52
trans-1,2-dichloroethylene	45.3
ethyl alcohol	2.7

About 52 parts by weight of HFE 7100, about 45.3 parts by weight of a chlorinated solvent consisting of trans-1,2-dichloroethylene, and about 2.7 parts by weight of a high polarity solvent consisting of ethyl alcohol were combined in a vessel at room temperature to form a liquid comparative cleaning composition.

Example C-2

The comparative cleaning composition of Example C-2 comprises 100% liquid n-propyl bromide.

The cleaning compositions of Examples 1, 2, C-1, and C-2 were evaluated for their ability to remove effectively various soils and for their compatibility with various substrates. These evaluations and the results thereof are described below.

Polypropylene injection molded parts were tested for compatibility with the compositions of Examples 1 and C-2. The polypropylene samples were not contaminated with any soils, but were tested for compatibility between the polypropylene and the cleaning compositions. The compatibility testing was performed in Branson BTC 200 vapor degreasers containing either the composition of Example 1 or Example C-2. The vapor degreaser contains two sumps, one with heat and one unheated with ultrasonics and condensing coils. Cleaning composition in the heated sump is heated to boiling. The vapor from the boiling composition condenses on the condensing coils and mixes with water extracted from the atmosphere. Water and condensate collect in a trough and pass to a water separator. Water is removed by the water separator (it floats to the top of the cleaning composition and is drained off). Pure cleaning composition overflows into the ultrasonic sump. Cleaning composition mixes with the soil removed by ultrasonic cleaning and "dirty" cleaning composition overflows into the boiling sump (all soil ends up in the boiling sump).

The following testing method was utilized. The samples were weighed on an analytical balance. For both compositions, the samples were lowered into the vapor above the boil sump for 1 minute, immersed in the rinse sump for the time indicated in the table, and then raised into the vapor for 20 seconds. The parts were then raised through the freeboard and out of the machine. Ultrasonics were used in the rinse sump for purposes of simulating cleaning when ultrasonics would be used to loosen adherent soils from the contaminated substrates.

For the composition of Example 1, the temperature of the rinse sump was 120°F (49°C) and the temperature of the boil sump and the vapor was 128°F (53°C). For the composition of Example C-2, the temperature of the rinse sump was 150°F

(66°C) and the temperature of the boil sump and the vapor was 158°F (70°C). The parts were weighed after completion of the testing and after weight loss stopped.

The results of the compatibility evaluations are illustrated in Table 4 below.

Table 4

	Cleaning Composition	Time in Rinse Sump (minutes)	Initial Weight (g)	Wt Change after Testing (g)	Final Weight Change (g)
A	Example 1	2	18.1132	+0.0271	+0.0055
B	Example 1	60	18.1364	+0.3594	+0.1296
C	Example C-2	2	18.0561	+0.4201	+0.0722
D	Example C-2	60	18.0334	+4.1474	+0.8169

The samples which were immersed in the cleaning composition of the present invention, Example 1, gained very little weight and showed no signs of degrading. The samples which were immersed in the comparative cleaning composition of Example C-2 gained more weight, and one of these samples, sample D, turned gray at the mold injection point. The above results illustrate that the composition of the present invention is more compatible with the polypropylene parts than the comparative composition of Example C-2.

Another possible substrate, Tecoflex tubes made of polyurethane, were tested for compatibility with the composition of Example 1. The compatibility testing was performed in a Branson BTC 200 vapor degreaser containing the composition of Example 1. The following method was utilized.

The Tecoflex tubes were cut into small sections and weighed. They were then fixtured in a wire mesh basket. The basket was lowered into the rinse sump for the time indicated in the table, raised into the vapor for 20 seconds, and then raised through the freeboard and out of the machine. The temperature of the rinse sump was 124°F (51°C); the temperature of the boil sump and the vapor was 128°F (53°C). Ultrasonics were used in the rinse sump for each test. The

samples were weighed immediately after completion of the testing and again after three hours.

The results of these tests are illustrated in Table 5 below.

Table 5

Cleaning Time (minutes)	Initial Weight (g)	Wt Change after Testing (g)	Wt Change after 3 hours (g)
1	1.6110	+0.0871	+0.0350
1	1.6365	+0.0815	+0.0361
1	1.5767	+0.0699	+0.0326
1	1.5431	+0.0642	+0.0319
2	1.5605	+0.1027	+0.0411
2	1.6261	+0.1004	+0.0429
2	1.5936	+0.0937	+0.0422
2	1.5525	+0.0854	+0.0415
10	1.6165	+0.2547	+0.1388
10	1.5472	+0.2374	+0.1338
10	1.6251	+0.2450	+0.1424
10	1.5866	+0.2420	+0.1418

Although the tubes softened slightly, they returned to their original hardness after three hours. The above results illustrate that the composition of the present invention is compatible with the Tecoflex tubes tested as the samples gained very little weight and showed no signs of degrading.

Additional Tecoflex tubes made of polyurethane were tested for compatibility with the composition of Example 1. The compatibility testing was performed in a Branson 125 vapor degreaser containing the composition of Example 1. The following method was utilized for testing.

The tubes were cut into small sections and weighed. They were then fixtured in a wire mesh basket. The basket was lowered into the vapor above the boil sump for 1 minute, then immersed in the rinse sump for 2 minutes, then raised into the vapor for 20 seconds, and finally raised through the freeboard and out of the machine. The rinse sump temperature was 105°F (41°C); the boil sump and vapor temperature was

128°F (53°C). Ultrasonics were used in the rinse sump. The tubes were weighed immediately after testing and again after weight loss stopped.

The results of these tests are illustrated in Table 6 below.

Table 6

Initial Weight (g)	Wt Change after Testing (g)	Final Weight Change (g)
2.2624	+0.1270	+0.0310
2.0767	+0.1069	+0.0260
2.1400	+0.1014	+0.0228
2.3562	+0.1154	+0.0279

Although the tubes swelled and softened slightly immediately after testing, they returned to their original hardness and close to their original weight. Additionally, none of the tube material leached out into the composition of Example 1. Accordingly, the above results illustrate that the composition of the present invention is compatible with the Tecoflex tubes tested as the samples gained very little weight and showed no signs of degrading.

The "swelling" characteristics of the composition of the present invention can be used to advantage in the following type of application. Plastic tubing, for example, silicone or polyurethane tubing, is soaked in the composition to increase its diameter. Then the tubing is placed over a needle, wire, or some other object of smaller diameter. The tubing shrinks around the wire to fit snugly, for example, in less than 25 minutes. An example of an application in which this swelling/shrinking process can be used is one involving medical tubing.

Additional possible substrates, catheters with hubs made of pellethane polyurethane and lumens made of tecothane polyurethane, were tested for compatibility with the compositions of Examples 1 and C-1. The catheter samples were contaminated with silicone oil. Cleaning and compatibility testing were performed in a Branson BTC 200 vapor degreasers containing either the composition of Example

1 or the composition of example C-1. The following method was utilized.

The samples were weighed on an analytical balance and were then fixtured in a wire mesh basket. The basket was lowered into the rinse sump for the time indicated in the table, raised into the vapor for 20 seconds, and then raised through the freeboard and out of the vapor degreaser.

For the composition of Example 1 the temperature of the boil sump and the vapor was 130°F (54°C) and the temperature of the rinse sump was 123°F (51°C). For the composition of Example C-1, the temperature of the boil sump and the vapor was 110°F (43°C) and the temperature of the rinse sump was 95°F (35°C). Ultrasonics were not utilized in the vapor degreaser for these tests.

After testing the parts were inspected for residual solvent and soil as well as any physical changes. When the weight stabilized a final weight reading was taken. The results of these tests are illustrated in the tables below. For the test results of Table 7, the cleaning composition of the present invention of Example 1 was utilized. For the test results of Table 8, comparative cleaning composition of Example C-1 was utilized.

Table 7 - Cleaning Composition of Present Invention

Rinse Sump Time (mins)	Initial Weight (g)	Final Weight Change (g)	Comments
2	6.6283	+0.0408	parts fixtured vertically in basket; no fading
2	6.9542	+0.0685	parts fixtured vertically in basket; no fading
2	6.9442	+0.0531	parts fixtured vertically in basket; no fading
2	6.8989	+0.0357	parts fixtured vertically in basket; no fading

Table 8 - Comparative Cleaning Composition

Rinse Sump Time (mins)	Initial Weight (g)	Final Weight Change (g)	Comments
2	6.9441	+0.2174	red and blue tips faded
2	7.0349	+0.2152	red and blue tips faded
2	6.8814	+0.2032	red and blue tips faded
2	6.9118	+0.0612	parts fixtured vertically in basket; red and blue tips faded
2	6.6140	+0.0592	parts fixtured vertically in basket; red and blue tips faded
2	6.6660	+0.0593	parts fixtured vertically in basket; red and blue tips faded
2	6.9167	+0.0612	parts fixtured vertically in basket; red and blue tips faded
4	6.8261	+0.2560	red and blue tips faded
4	7.0098	+0.2481	red and blue tips faded
4	6.8534	+0.2438	red and blue tips faded

Both the cleaning composition of the present invention (Example 1) and the comparative composition (Example C-1) cleaned the catheters well. The comparative cleaning composition, however, attacked the catheters, as it caused the color in the tips to fade. The cleaning composition of the present invention cleaned well and was compatible with the catheters, as it caused no fading of color.

Another substrate in accordance with the present invention, round metal lids coated with varnish which were cut into small samples, were tested at elevated temperatures for compatibility with the compositions of Examples 1 and C-1. The testing was performed by immersing the samples in rinse sumps of Branson BTC 200 vapor degreasers which contain either Example 1 or Example C-1. The following method was utilized.

The varnish samples were weighed on an analytical balance and were then immersed in the rinse sump of the vapor degreaser. The temperature of the rinse sump containing the

composition of Example C-1 was 105°F (41°C) and the temperature of the rinse sump containing the composition of Example 1 was 123°F (51°C). After 10 minutes or 60 minutes, as indicated in the table, the samples were removed from the rinse sump, weighed, and inspected for any physical changes.

The results of the compatibility evaluations are illustrated in Table 9 below.

Table 9

Cleaning Comp	Varnish	Time (min)	Initial Wt (g)	Change in Wt(g)	Observations
Ex 1	B-185	60	3.8126	+0.0341	
Ex 1	B-185	10	3.9551	+0.0112	
Ex C-1	B-185	60	6.5497	-0.0065	edge area attacked
Ex C-1	B-185	10	6.1599	-0.0102	edge area attacked
Ex 1	U-372	60	3.8647	+0.0039	
Ex 1	U-372	10	5.9916	+0.0199	
Ex C-1	U-372	60	5.3917	+0.0294	edges peeling slightly
Ex C-1	U-372	10	4.3865	+0.0314	

The results documented above illustrate that the composition of Example 1 is more compatible with the varnishes tested than is the comparative composition of Example C-1, as the comparative composition attacked the varnish coated lids.

Another substrate suitable for cleaning with the cleaning composition of the present invention, hardened globules of polyurethane (Solithane 113/Hughes), was tested for compatibility with the compositions of Examples 1 and C-1. Most of the globules were attached to aluminum foil to test the adhesive properties of the polyurethane after being subjected to the cleaning compositions. The testing was performed by immersing the samples in rinse sumps of Branson BTC 200 vapor degreasers which contained the composition of either Example 1 or Example C-1. The following method was utilized.

The samples were weighed on an analytical balance and were then immersed in the rinse sump of the vapor degreaser.

The temperature of the rinse sump containing the composition of Example C-1 was 100°F (38°C) and the temperature of the rinse sump containing the composition of Example 1 was 122°F (50°C). After 10 minutes or 60 minutes, the samples were removed from the rinse sump, weighed and inspected for any physical changes. The results of these compatibility evaluations are documented in the following table.

Table 10

Cleaning Comp	Time (mins)	On Foil	Initial Wt (g)	Change in Wt(g)	Observations
Ex 1	60	yes	0.2662	+0.0510	stayed adhered to foil
Ex 1	60	yes	0.1898	+0.0385	stay adhered to foil
Ex 1	60	yes	0.2121	+0.0379	stayed adhered to foil
Ex 1	10	yes	0.4182	-0.013	stayed adhered to foil
Ex 1	10	no	0.2120	+0.0225	
Ex C-1	60	yes	0.2631	X	became brittle and fell apart
Ex C-1	60	yes	0.2485	X	became brittle and fell apart
Ex C-1	10	yes	0.2621	0.0399	stayed adhered to foil
Ex C-1	10	no	4.9141	-0.0051	

The results of the table above illustrate that the polyurethane is compatible with the composition of Example 1 for both short and long exposure times. The polyurethane is not compatible with the composition of Example C-1 for long exposure times, as the polyurethane fell apart after exposure to the comparative composition for 60 minutes.

The composition of Example 1 was tested for its ability to clean silicone soils (DC-510 and DC-200) from glass plates. The cleaning tests were performed in a Branson BTC 200 vapor degreaser containing the composition of Example 1. The following method was utilized.

Glass specimen plates were cleaned with acetone and dipped in the sample of silicone. The plates were then fixtured in a wire mesh basket. The basket was lowered into

the rinse sump of the vapor degreaser for the time indicated in the following tables, then raised into the vapor for 20 seconds, and finally raised through the freeboard and out of the machine. The temperature of the rinse sump of the composition of Example 1 was 124°F (51°C). The results of these cleaning evaluations are illustrated in the chart below.

Table 11

Cleaning Comp	Soil	Time in Rinse Sump (mins)	Results
Ex 1	DC-510	5	clean
Ex 1	DC-510	3	clean
Ex 1	DC-510	1	clean
Ex 1	DC-200	5	clean
Ex 1	DC-200	3	clean
Ex 1	DC-200	1	clean

The above results illustrate that the composition of Example 1 is effective in removing silicone soils from contaminated glass substrates.

The next example is illustrative of a composition which is within the scope of the present invention and which includes a non-volatile functional material.

Example 3

A composition comprising 2 wt.% of Dow Corning 360 polydimethylsiloxane fluid, 52.9 wt.% of 3M HFE 7100, 35.3 wt.% of octamethyltrisiloxane, and 9.8 wt.% of isopropyl alcohol was formulated. Stainless steel surgical scalpel blades were immersed into the composition in a pan at room temperature. The blades were removed from the pan and allowed to set for about 30 minutes, after which all of the volatile constituents of the composition evaporated. A lubricating film of silicone film in continuous form and having a thickness of about 1 to 2 mils (0.001 to 0.002 inch) remained on the blades.



What is claimed is:

1. An azeotropic nonflammable liquid composition which has cleaning properties, which is substantially free of a chlorinated hydrocarbon solvent, and which has an ozone depletion factor of no greater than about 0.15 and which comprises the following volatile constituents, each of which has an ozone depletion factor of no greater than about 0.15:

- (a) a liquid nonflammable fluorinated compound;
- (b) a low polarity solvent which is capable of dissolving no greater than about 10% water by volume; and
- (c) a high polarity solvent which is capable of dissolving at least about 10% water by volume.

2. The composition of claim 1 wherein the fluorinated compound is selected from the group consisting of fluorocarbons, hydrofluorocarbons, fluoroethers, and hydrofluoroethers.

3. The composition of Claim 2 wherein the fluorinated compound comprises a hydrofluoroether.

4. The composition of Claim 1 wherein the fluorinated compound is partially fluorinated.

5. The composition of claim 1 wherein the low polarity solvent is selected from the group consisting of n-propyl bromide, terpenes, polymethylsiloxanes, and petroleum solvents.

6. The composition of claim 5 wherein the low polarity solvent comprises n-propyl bromide.

7. The composition of Claim 5 wherein the low polarity solvent comprises octamethyltrisiloxane.

8. The composition of claim 1 wherein the high polarity solvent is selected from the group consisting of low molecular weight alcohols and low molecular weight glycol ethers.

9. The composition of Claim 8 wherein the low molecular weight alcohols have from 1 to 4 carbon atoms.

10. The composition of Claim 9 wherein the low molecular weight alcohol is isopropyl alcohol.



11. The composition of Claim 1 comprising a hydrofluoroether, n-propyl bromide, and isopropyl alcohol.

12. The composition of Claim 1 comprising a hydrofluoroether, octamethyltrisiloxane, and isopropyl alcohol.

13. The composition of Claim 1 which has an ozone depletion factor of no greater than about 0.05 and which comprises:

- (a) from about 50 wt.% to about 80 wt.% of a liquid nonflammable fluorinated compound with an ozone depletion factor of no greater than about 0.05;
- (b) from about 15 wt.% to about 40 wt.% of a liquid low polarity solvent which is capable of dissolving no greater than about 10% water by volume and which has an ozone depletion factor of no greater than about 0.05; and
- (c) from about 3 wt.% to about 12 wt.% of a liquid high polarity solvent which is capable of dissolving at least about 10% water by volume and which has an ozone depletion factor of no greater than about 0.05.

14. The composition of claim 13 wherein the fluorinated compound is selected from the group consisting of fluorocarbons, hydrofluorocarbons, fluoroethers, and hydrofluoroethers.

15. The composition of claim 13 wherein the low polarity solvent is selected from the group consisting of n-propyl bromide, terpenes, polymethylsiloxanes, and petroleum solvents.

16. The composition of claim 13 wherein the high polarity solvent is selected from the group consisting of low molecular weight alcohols and low molecular weight glycol ethers.

17. The composition of claim 13 comprising about 70 wt.% 1-methoxy-nonafluorobutane, about 25 wt. % n-propyl bromide, and about 5 wt.% isopropyl alcohol.

18. The composition of Claim 13 comprising about 54 wt.% 1-methoxy-nonafluorobutane, about 36 wt.% octamethyltrisiloxane, and about 10 wt.% isopropyl alcohol.



19. A process for removing adherent soils from a soiled substrate comprising:

(a) contacting the soiled substrate with an azeotropic nonflammable liquid cleaning composition which is compatible with the substrate for a time sufficient to remove the adherent soils, the cleaning composition being substantially free of a chlorinated hydrocarbon solvent and having an ozone depletion factor of no greater than about 0.15 and comprising:

(i) a liquid nonflammable fluorinated compound with an ozone depletion factor of no greater than about 0.15;

(ii) a liquid low polarity solvent which is capable of dissolving no greater than about 10% water by volume and which has an ozone depletion factor of no greater than about 0.15; and

(iii) a liquid high polarity solvent which is capable of dissolving at least about 10% water by volume and which has an ozone depletion factor of no greater than about 0.15; and

(b) removing the substrate from the liquid cleaning composition.

20. The process of claim 19 wherein the soiled substrate is contacted with the nonflammable cleaning composition by immersing the substrate in the cleaning composition at room temperature.

21. The process of claim 19 wherein the soiled substrate is contacted with the nonflammable cleaning composition by spraying the cleaning composition onto the soiled substrate.

22. The process of claim 19 further comprising the following steps:

(a) heating the liquid cleaning composition to its boiling point to form a vapor phase which overlies the boiling liquid cleaning composition, the vapor phase comprising the nonflammable fluorinated compound, the low polarity solvent, and the high



polarity solvent, each present in the same proportion as present in the boiling liquid composition;

- (b) contacting the soiled substrate with the boiling cleaning composition;
- (c) withdrawing the substrate from the boiling cleaning composition and into the vapor phase;
- (d) contacting the substrate with the vapor phase; and
- (e) withdrawing the substrate from the vapor phase.

23. A composition of Claim 1 including a non-volatile functional material dissolved in the composition.

24. A composition of Claim 23 wherein said material is a liquid at room temperature.

25. A composition of Claim 23 wherein said material is a solid at room temperature.

26. A method for depositing a non-volatile functional material on a surface comprising applying to said surface a composition according to Claim 23, forming on said surface a deposit which includes said material and which is free of each of said fluorinated compound, low polarity solvent, and high polarity solvent by effecting evaporation of each of said fluorinated compound, low polarity solvent, and high polarity solvent.

27. A composition according to Claim 1 wherein said low polarity solvent is capable of dissolving no greater than about 0.1% water by volume.

28. A process according to Claim 19 wherein said low polarity solvent is capable of dissolving no greater than about 0.1% water by volume.

29. A composition according to Claim 1 which is plastic-compatible.

30. A process according to Claim 19 wherein said composition is plastic-compatible.