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NOVEL DRY CLEANING MIXTURE

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ABSTRACT OF THE DISCLOSURE

Mixtures comprising water, tertiary amyl alcohol and tetrachlorodifluoroethane which, over substantially the entire course of their evaporation or distillation, form azeotropic non-flammable vapors containing tertiary amyl alcohol and tetrachlorodifluoroethane. These mixtures are useful in dry cleaning textile fabrics and fibers with reduced hazard of fire.

BACKGROUND OF THE INVENTION

It has been suggested to employ volatile mixtures of lower aliphatic alcohols and halogenated hydrocarbons in cleaning compositions. However, many of the possible mixtures of lower aliphatic alcohols and halogenated hydrocarbons suffer from at least one disadvantage which prevents or seriously limits their use in the dry cleaning of textile fabrics and fibers.

In conventional dry cleaning of textile fabrics and fibers, the textile, after being contacted with the liquid cleaning mixture, is dried by allowing the cleaning mixture adhering to the textile to evaporate. Furthermore, spent cleaning mixture, that is cleaning mixture saturated with soils removed from the textile, is usually distilled to recover the constituents of the mixtures devoid of soils and non-volatile cleaning adjuvants such as detergents.

However, many of the possible mixtures of lower aliphatic alcohols and halogenated hydrocarbons evaporate or distill to produce flammable alcohol containing vapors. Use of such flammable vapor-producing mixtures in textile dry cleaning constitutes a serious fire hazard.

It is an object of the present invention to devise novel alcoholic halogenated hydrocarbon mixtures which distill or evaporate with reduced hazard of fire.

This and additional objects and advantages will be apparent from the following description of my invention.

SUMMARY OF THE INVENTION

The above objects are attained and the aforementioned disadvantages of prior art alcoholic-halogenated hydrocarbon mixtures are overcome, according to the invention, in mixtures which are useful in cleaning textile fabrics and fibers and which comprise about 87.0 to about 88.9 weight percent tetrachlorodifluoroethane, about 7.0 to about 11.0 weight percent tertiary amyl alcohol and about 0.1 to about 6 weight percent water. The invention also includes a process of cleaning of textile fabrics and fibers such as those of wool, cotton, rayon, the nylons including polyhexamethylene adipamide and polyepsilon caprolactam, polyesters including cellulose acetate, cellulose triacetate and polyethylene terephthalate, and polyacrylonitrile, with the novel mixtures of the invention.

The cleaning mixtures of the invention are surprisingly effective in removing stains of both the water-soluble and organic solvent soluble type from textile fabrics and fibers.

The cleaning mixtures of the invention are critically characterized in the prescription of concentrations therein of tetrachlorodifluoroethane, tertiary amyl alcohol and water so that the present mixture, over substantially the entire course of its evaporation or distillation at atmospheric pressure, forms non-flammable vapors of constant boiling mixtures, that is azeotropes, containing the flammable tertiary amyl alcohol together with tetrachlorodifluoroethane. I have unexpectedly discovered that on distillation (or evaporation) of the present mixture the water component of the mixture is evolved as a vapor containing about 87.2 weight percent tetrachlorodifluoroethane, about 7.5 weight percent tertiary amyl alcohol and about 5.3 weight percent water which mixture boils at constant composition in the vapor and liquid phase at 74–75° C. at atmospheric pressure, that is, a pressure of about 760 mm. of mercury. After removal of the water component, the remaining tertiary amyl alcohol and tetrachlorodifluoroethane of the mixture distill (or evaporate) to give a vapor containing about 11.4 weight percent of the tertiary amyl alcohol and about 88.6 weight percent of the tetrachlorodifluoroethane which mixture boils at constant composition in the vapor and liquid phase at a temperature in the range of about 89.0 to 89.7° C. at atmospheric pressure. Surprisingly vapors of both the tetrachlorodifluoroethane - tertiary amyl alcohol - water azeotrope and the tertiary amyl alcohol-tetrachlorodifluoroethane azeotrope are substantially non-flammable. Accordingly, the fire-hazard in distillation or evaporation of the present mixture is greatly diminished as compared to the hazard encountered with aqueous alcoholic halogenated hydrocarbon mixtures which do not evolve non-flammable azeotropic vapors over the entire course of their distillation or evaporation. Furthermore, the present azeotropic compositions are found to boil at lower temperatures than the pure tetrachlorodifluoroethane, tertiary amyl alcohol and water components of the present mixture, that is, are azeotropic compositions of the minimum boiling type. Accordingly, in the cleaning of textiles, the formation of such minimum boiling azeotropic compositions on distillation or evaporaton of the present mixture facilitates both evaporation of adherent cleaning mixture from the cleaned textile substrate and the recovery of the cleaning mixture by distillation as compared to the evaporation or recovery by distillation of either the pure components of the present mixture or of aqueous tertiary amyl alcohol-tetrachlorodifluoroethane mixtures which do not form azeotropic vapors over the entire course of their distillation or evaporation.

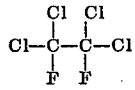
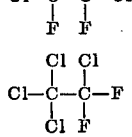
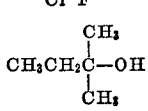
DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS THEREOF

The present novel mixtures are prepared by mixing water, tertiary amyl alcohol and tetrachlorodifluoroethane in the prescribed amounts according to conventional techniques.

The tetrachlorodifluoroethane component of the present mixtures is available commercially as a mixture of the symmetrically-substituted isomer, 1,1,2,2-tetrachloro-2,2-difluoroethane and the asymmetrically substituted isomer, 1,1,1,2-tetrachloro-2,2-difluoroethane in a mol ratio of about 69:31. The melting and boiling points of the two tetrachlorodifluoroethane isomers are compared with

those of the other components of the present cleaning mixture in Table I below.

TABLE I

Compound	Formula	Melting point, ° C.	Boiling point, ° C. at 760 mm.
1,1,2,2-tetrachloro-1,2-difluoroethane (American Society of Refrigerating Engineers Designation 112).		23.5	92.8
1,1,1,2-tetrachloro-2,2-difluoroethane (American Society of Refrigerating Engineers Designation 112a).		40.6	91.0
Tertiary amyl alcohol			92.8
Water	H_2O	0	100.0

The azeotropes of tertiary amyl alcohol or aqueous tertiary amyl alcohol with either pure isomer of tetrachlorodifluoroethane have approximately the same composition, normal boiling point and properties as the corresponding azeotropes with mixtures of the pure isomers. Accordingly, my invention includes tetrachlorodifluoroethane-containing mixtures derived from either the symmetrically-substituted or asymmetrically-substituted tetrachlorodifluoroethane or from mixtures of these isomers. Hence, reference in this specification and the claims appended hereto to "tetrachlorodifluoroethane," unless otherwise indicated, is intended to include the pure isomers and/or any mixtures thereof. However, the aforementioned commercial mixture of tetrachlorodifluoroethane isomers, because of its ready availability, is the preferred tetrachlorodifluoroethane component of the invention.

The present cleaning mixture contains about 0.1 to about 6.0 weight percent water to solubilize textile soils which are soluble in water but insoluble in the organic components of the present mixture. Preferably, the concentration of water in the novel cleaning mixture is maintained at about 0.1 to about 1.0 weight percent to diminish shrinkage in cleaning wool-containing fabrics or to diminish wrinkling of rayon-containing fabrics. An especially good cleaning result is achieved in employing a mixture of the invention containing about 1.0 weight percent water.

The novel water-tertiary amyl alcohol-tetrachlorodifluoroethane mixtures of the invention are substantially inert to synthetic organic textile fabrics and fibers such as nylon, polyacrylonitrile, and polyester and do not appreciably dissolve or swell these substances. Additionally, the present composition is non-toxic and substantially non-corrosive to metals such as aluminum and stainless steel, even on contact with such metals for periods as long as one month.

The process of cleaning textile fabrics and fibers with the novel water tertiary amyl alcohol tetrachlorodifluoroethane mixtures of the invention is carried out by contacting the soiled textile fabric with the novel mixture in the liquid phase employing conventional techniques, apparatus and conditions.

For example, in the present process the conditions of cleaning temperature and contact time, the proportions of cleaning mixture and textile fabric and the distillation techniques for recovery of spent cleaning mixture are susceptible to wide variation but are conventional in the dry cleaning art.

In accord with conventional dry cleaning procedures, the cleaning of textiles with the present novel mixture is advantageously effected in the presence of an organic detergent which may be either dissolved or dispersed in the cleaning mixture. The particular type and structure of the organic detergent is not critical and any of a wide variety of non-volatile organic detergents can be employed in the present process including, for example, Aerosol OT, a dioctyl ester of sodium sulfosuccinic acid (an anionic detergent manufactured by The American Cyanamide Co.), Igepal CO–730, a nonyl phenoxypoly (ethyleneoxy) ethanol (a non-ionic detergent manufactured by General Aniline and Film Corp.) and Emcol P10–59, an amine salt of dodecyl benzene sulfonic acid (an anionic detergent manufactured by Witco Chemical Corp.).

The concentration of the detergent in the cleaning mixture is also not critical and can be varied over a wide range depending, in general, upon the particular type of detergent employed. An especially good result is achieved in the present cleaning process in employing an anionic-type organic detergent at a concentration of about 1 to about 2 weight percent of the cleaning mixture.

It will be apparent to those skilled in the art that other additives, which for specialized purposes are conventionally incorporated into dry cleaning mixtures, can also be incorporated into the present novel mixtures, including for example, textile lubricants, textile water-proofing agents, moth-proofing agents, soil release agents and the like.

In the following examples which serve to illustrate my invention, percentages and proportions are by weight unless otherwise noted and temperatures are in degrees centigrade.

EXAMPLE 1

Preparation of tertiary amyl alcohol-tetrachlorodifluoroethane azeotrope

Part A.—A mixture of 60 g. of tertiary amyl alcohol and 240 g. of tetrachlorodifluoroethane (a commercially available mixture consisting of about 69 mol percent $CFCl_2CFCl_2$ and about 31 mol percent CCl_3CF_2Cl) is heated to reflux in a conventional laboratory fractional distillation apparatus. After equilibrium is attained, the mixture is partially distilled to collect consecutively the fractions listed in Table II below.

TABLE II

Fraction	Boiling point at 760 mm. (still head temperature at which fraction is collected)	Weight of fraction, g.
Forerun	84–88°	5.3
First fraction	88–89°	39.5
Second fraction	89°	214.5

On redistillation the major dsitillate fraction, that is, the second fraction above, shows no change in boiling point at a pressure of 760 mm. of mercury or in composition. This constant boiling fraction, as analyzed by vapor phase chromatography, is found to have the following composition:

	Weight percent
Tetrachlorodifluoroethane	88.6
Tertiary amyl alcohol	11.4

This fraction when tested for flammability according to the Tag Open Cup Flash Point Test of Volatile Flammable Materials (ASTM–D–1310–63) is found to be non-flammable.

Part B.—Repetition of the procedure set out in Part A, above, but substituting an equivalent amount of substantially pure (99 mol percent) 1,1,2,2-tetrachloro-difluoroethane for the tetrachlorodifluoroethane isomer mixture charged in Part A gives a non-flammable binary azeotrope of the alcohol and the halogenated hydrocarbon which boils at 89.2° at a pressure of 760 mm. mercury and which contains substantially the same proportions of tertiary amyl alcohol and halogenated hydrocarbon as the constant boiling mixture obtained in Part A.

Part C.—Repetition of the procedure set out in Part A, above but substituting an equivalent amount of substantially pure (97 mol percent) 1,1,2,2-tetrachloro-2,2-difluoroethane for the tetrachlorodifluoroethane isomer mixture charged in Part A gives a non-flammable binary azeotrope of the alcohol and halogenated hydrocarbon which boils at 89.7° and which contains substantially the same proportions of tertiary amyl alcohol and halogenated hydrocarbon as the constant boiling mixture obtained in Part A.

The foregoing results indicate that azeotropic mixtures formed in accordance with the invention from substantially pure tetrachlorodifluoroethane isomers or from mixtures of these isomers have substantially identical compositions and have no significant difference in properties.

EXAMPLE 2

Preparation of water-tertiary amyl alcohol tetrachlorodifluoroethane azeotrope

A mixture of 50 g. of tertiary amyl alcohol, 20 g. of water and 50 g. of the tetrachlorodifluoroethane isomer mixture of Example 1 is heated to reflux in the fractional distillation apparatus of Example 1. After equilibrium is established, the mixture is distilled at a still head temperature of 74–75° at 760 mm. pressure to give about 60 g. of distillate which on redistillation shows no change in boiling point or composition. This distillate as analyzed by vapor phase chromatography is found to possess the following composition:

	Weight percent
Tetrachlorodifluoroethane	87.2
Tertiary amyl alcohol	7.5
Water	5.3

The distillate of the above-defined composition is tested for flammability according to the Tag Open Cup Flash Point Test of Volatile Flammable Materials (ASTM–D–1310–63) and is found to be non-flammable.

Substantially identical results are obtained on repeating the foregoing procedure with either substantially pure (99 mol percent) 1,1,2,2 - tetrachloro - 1, 2-difluoroethane or substantially pure (97 mol percent) 1,1,1,2-tetrachloro-2,2-difluoroethane in place of the aforementioned tetrachlorodifluoroethane isomer mixture.

EXAMPLE 3

A test set of four 2.5" x 7" swatches of rayon fabric (National Institute of Dry Cleaning White Rayon Test fabric) are each spotted by one of the following stains:

Lipstick
Catsup
Mustard
Lanolin

The stains are allowed to dry and to "set" for 24 hours at room temperature. A duplicate set of four stained rayon swatches are similarly prepared for use as a control. Each soiled swatch of the test set is then immersed for 30 minutes at room temperature (about 25°) in 200 cc. of agitated cleaning bath consisting of:

About 98 weight percent of a mixture of 11.4 weight tertiary amyl alcohol and 88.6 weight percent of commercial tetrachlorodifluoroethane wherein the mol ratio of $CFCl_2CFCl_2$ and CCl_3CClF_2 is about 69:31.
About 1 weight percent water
About 1 weight percent of a dodecyl benzene sulfonic acid, amine salt anionic oil-soluble detergent. (Emcol P10–59, Witco Chemical Corp.).

Each swatch is raised from the bath, squeezed to express cleaning mixture and allowed to stand in the air at room temperature for 30 minutes to evaporate adherent cleaning mixtures. The cleaned test swatches are devoid of wrinkles.

The effectiveness of stain removal by the foregoing cleaning procedure is rated by visual comparison of the cleaned test swatches employing a rating scale of 1 to 10 with 1 being substantially about 10% stain removal and 10 being substantially complete stain removal, that is, about 100% stain removal. That portion of each test swatch which had not been originally stained is compared with the like portion of the corresponding control swatch to evaluate redeposition of stain during the cleaning operation. Redeposition of stain as indicated by discoloration of the fabric is rated according to the following ascending scale: slight, moderate, severe. The results of this experiment are summarized in Table III below.

TABLE III

Stain removal rating (percent stain removed ×10):	
Lipstick	9.
Catsup	9.
Mustard	8.
Lanolin	10.
Stain redeposition	Slight.

The foregoing results wherein from about 80 to 100% of stain is removed by the present mixtures with only slight restaining of the fabric swatches are indicative of the surprising cleaning efficiency of the present mixture.

I claim:

1. A mixture consisting essentially of about 87.0 to about 88.9 weight percent tetrachlorodifluoroethane, about 7.0 to about 11.0 weight percent tertiary amyl alcohol and about 0.1 to about 6.0 weight percent water.

2. A mixture as defined in claim 1 containing about 0.1 to about 1.0 weight percent water.

3. A mixture as defined in claim 1 wherein the tetrachlorodifluoroethane is a mixture of 1,1,2,2-tetrachloro-1,2-difluoroethane and 1,1,1,2-tetrachloro-2,2 - difluoroethane in a mol ratio of about 69:31.

4. A mixture as defined in claim 3 containing about 1.0 weight percent water.

5. A mixture as defined in claim 1 which boils at substantially constant composition in vapor and liquid phase at 74° to 75° C. under atmospheric pressure and which contains about 87.2 weight percent tetrachlorodifluoroethane, about 7.5 weight percent tertiary amyl alcohol and about 5.3 weight percent water.

6. A mixture as defined in claim 5 wherein the tetrachlorodifluoroethane is a mixture of 1,1,2,2-tetrachloro-1,2-difluoroethane and 1,1,1,2-tetrachloro-2,2 - difluoroethane in a mol ratio of about 69:31.

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U.S. Cl. X.R.

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