United States Patent Office 3,836,474
Patented Sept. 17, 1974

3,836,474

NOVEL NON-FLAMMABLE AZEOTROPE SOLVENT COMPOSITIONS

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No Drawing. Continuation of application Ser. No. 77,388, Oct. 1, 1970, now Patent No. 3,692,686. This application July 10, 1972, Ser. No. 270,136
The portion of the term of the patent subsequent to Sept. 19, 1989, has been disclaimed
Int. Cl. C11d 7/50
U.S. Cl. 252—171 4 Claims

ABSTRACT OF THE DISCLOSURE

Tetrachlorodifluoroethane (sym.-, asym.-, and mixtures thereof) nitromethane, water and isopropanol or secondary butanol form quaternary azeotropic mixtures which are useful as dry cleaning solvents and are particularly useful for the removal of hard-to-remove stains from leather.

BACKGROUND OF THE INVENTION

This is a continuation of application Ser. No. 77,388, filed Oct. 1, 1970, now U.S. Pat. 3,692,686.

In conventional dry cleaning processes for the removal of dirt, grease and various soils from textile and leather articles, use is made of organic solvents having dissolved therein a detergent in minor amounts. The dry-cleaning bath may also contain other additives such as water, textile softeners, water repellents and the like.

Solvents commonly used as the organic components of such dry cleaning compositions include saturated aliphatic hydrocarbons such as Stoddard solvent, gasoline or other low boiling paraffinic hydrocarbons; low-boiling aromatic hydrocarbons, such as benzene, toluene, and xylene; and low-boiling polyhalogenated hydrocarbons of 1 to 2 carbon atoms such as carbon tetrachloride, methyl chloroform, trichloroethylene, tetrachloroethylene, trichlorofluoromethane, dichlorotrifluoroethane, trichlorodifluoroethanes, and mixtures of these.

Numerous anionic, cationic, and nonionic detergents have been used as additives to the dry cleaning compositions. Such additives, are known to have adverse effects when contacted with leather articles in that they remove the natural oil or grease from the leather leaving it harsh and brittle.

Other candidate solvent compositions, although having satisfactory solvency characteristics, are flammable and/or toxic, thereby creating hazards to personnel in their use. In addition, because of the diverse character of the many stains and soils encountered and the many different types of textiles, both natural and synthetic, which are encountered by dry cleaning establishments, much dry cleaning must practically be carried out on a custom basis and requires hand spotting to remove deep stains.

The stains encountered in the dry cleaning process can be broadly categorized as organic solvent-soluble and water-soluble. Thus, grease and oil stains can be effectively removed by organic solvents such as perchloroethylene, while catsup, perspiration, common dirt stains and the like are removed by water. Since both types of stains or soils are usually present on garments and the like submitted for dry cleaning, it would be desirable to include both organic solvents and water in the dry cleaning liquor. Since water and the common dry cleaning solvents are not mutually soluble to any useful extent, it is general practice in this art, as noted above, to utilize emulsifying agents, such as alkylaryl sulfonates, to increase the water tolerance of the organic solvents. To obtain an effective increase in the water tolerance of many dry cleaning solvents requires

the use of relatively large proportions of emulsifying agent. This not only increases the cost of the solvent mixture but also such large proportions of emulsifying agent adversely affect the material being cleaned, for example, by removing natural oils, sizing agents, water proofing resins, and the like. Moreover, many textile materials are sensitive to excessive moisture. Wool, for example, may shrink, and rayon and certain synthetics may wrinkle when cleaned with solvents containing excessive moisture. A delicate balance between organic solvents and water must be maintained.

It is common practice to use polyhalogenated lower alkanes such as trichlorotrifluoroethane, tetrachlorodifluoroethane, and the like, for solvent cleaning of a variety of materials. Such compounds are notably of low toxicity for warm blooded animals and are non-flammable. However, such solvents are not entirely for use in dry cleaning of textile materials since no known single compound is an effective solvent for the wide variety of stains encountered.

A variety of solvent mixtures have been tested for such purposes but generally have been found to be lacking to a greater or lesser extent in one or more of the desired characteristics of dry cleaning mixtures. Such mixtures may contain two or more halocarbons or at least one halocarbon together with another organic compound such as an alcohol, ether, or ketone. In the usual instance, such mixtures are not constant boiling, that is they fractionate during use and during reclamation, losing one or more of the more volatile components. Such mixtures with altered compositions may have less desirable properties such as lower solvency for stains, less inertness towards textile materials and increased flammability.

A number of azeotropic mixtures have been suggested for cleaning of a variety of materials. Azeotropes do not suffer from the above discussed fractionation disadvantage possessed by non-constant boiling mixtures. Unfortunately, the solvency character of the known azeotropic compositions leave much to be desired when employed in the dry cleaning of most textile materials and, particularly, leather articles. Such compositions have very low tolerance for water and hence, while effective to remove oil-soluble stains, are ineffective to remove water-soluble stains.

Moreover, although azeotropic compositions possess the above described advantages over non-azeotropic (non constant boiling) compositions, as evidenced by the disclosure in U.S. Pat. 3,085,065 to Kvalnes, a basis has not been found for predicting the formation of azeotropes between or among halocarbons, much less mixtures of halocarbons and other organic compounds and/or water.

It is, therefore, a major object of this invention to provide novel solvent compositions for removing stains normally encountered on textile materials and leather which novel solvent compositions exhibit a high degree of solvency for such stains.

Another object of this invention is to provide novel solvent compositions which are constant boiling or essentially constant boiling.

Still another object is to provide novel solvent compositions containing an organic solvent and water which exhibit high solvency toward both oil-soluble and water-soluble stains.

SUMMARY OF INVENTION

In accordance with the present invention, we have discovered constant boiling mixtures which are highly effective dry cleaning solvents for removing common household stains, and which do not include a detergent compound. The novel constant boiling mixtures of our invention consist essentially of tetrachlorodifluoroethane, nitromethane, water and isopropanol or secondary butanol.

More particularly our invention includes the novel azeotropic mixtures consisting essentially of about 76.8 weight percent of tetrachlorodifluoroethane, about 9.3 weight percent of nitromethane, about 3.7 weight percent of water, and about 10.2 weight percent of isopropanol. These quaternary azeotropic mixtures of the invention boil at about 69.0° C. at 760 mm. pressure.

The invention also includes the novel azeotropic mixtures consisting essentially of about 78.6 weight percent of tetrachlorodifluoroethane, about 14.1 weight percent of nitromethane, about 4.7 weight percent of water, and about 2.6 weight percent of secondary butanol. These quaternary azeotropic mixtures of this invention boil at about 70.5° C. at 760 mm. pressure.

These novel solvent mixtures are constant boiling or essentially constant boiling and thus can be recovered after use by distillation without change in composition or solvent properties.

The novel solvent mixtures have been found to be effective cleaning compositions for leather and in use are contacted with the soiled leather for a period of time sufficient to effect substantially complete dissolution of the oil-soluble and water-soluble stains, such as catsup, can be removed without noticeably reducing the flexibility or softness ("hand") of the leather article.

The novel quaternary solvent mixtures of the invention on standing, separate into two layers. However we have found that the separated mixtures can be readily dispersed to uniform emulsions by gentle agitation and without recourse to emulsifying agents.

The lower layers which separate from the quaternary mixtures on standing are highly effective dry cleaning solvents for textile materials such as wool and in use are contacted with the soiled textile materials for a period of time sufficient to effect substantially complete dissolution of the oil-soluble and water-soluble stains. These lower layers contain only a minimum concentration of water and hence while effective for the removal of water-soluble stains, do not cause shrinkage of wool or wrinkling of rayon.

The lower layer obtained from the isopropanol containing azeotropes has the approximate composition of

	Wt. percent
Tetrachlorodifluoroethane	80.00
Isopropanol	9.7
Nitromethane	9.3
Water	1.0

This layer amounts to about 96% of the original quaternary azeotropic mixture.

The upper layer contains substantially none of the tetrachlorodifluoroethane. This layer contains about

	Wt. percent
Water	69.0
Isopropanol	22.2
Nitromethane	8.8

This layer, which amounts to about 4% of the azeotrope, may be drawn off and either discarded or admixed with additional tetrachlorodifluoroethane and the mixture distilled to recover an additional quantity of the quaternary azeotrope.

From the azeotropic mixtures containing secondary butanol the lower layer has the approximate composition of

	Wt. percent
Tetrachlorodifluoroethane	89.36
Sec.-butanol	2.0
Nitromethane	8.6
Water	0.04

This layer amounts to about 95% of the original quaternary azeotropic mixture.

The upper layer contains substantially none of the tetrachlorodifluoroethane. This layer contains about

	Wt. percent
Water	82.2
Sec. butanol	4.6
Nitromethane	13.2

This layer, which amounts to less than 5% of the azeotrope, may likewise be drawn off and either discarded or admixed with additional tetrachlorodifluoroethane and the mixture distilled to recover an additional quantity of the quaternary azeotrope.

The halocarbon component of the novel quaternary mixtures of the invention is available commercially as a mixture of about 69 mol percent of the symmetrical isomer, 1,1,2,2-tetrachloro-2,2-difluoroethane and about 31 mol percent of the asymmetrical isomer, 1,1,1,2-tetrachloro-2,2-difluoroethane. We have found that either isomer, per se, or the commercially available mixtures thereof, when admixed with nitromethane, secondary butanol or isopropanol and water, yield azeotropic mixtures of substantially identical characteristics and properties. Accordingly, all references contained in this specification to tetrachlorodifluoroethane apply to mixtures of the two isomers, in any proportions, or to either isomer, per se.

The following examples will illustrate the invention. Unless otherwise indicated, parts and percentages are by weight and temperatures are given in degrees centigrade.

Example 1.—Preparation of the Quaternary Azeotrope

(a) Equimolecular quantities of tetrachlorodifluoroethane (b.p. 92.8°), the commercially available mixture, isopropanol (b.p. 82.0°), nitromethane (b.p. 101.2°) and water (b.p. 100°) were charged to a still equipped with a fractionating column. This mixture was heated to reflux and then distilled. The fraction boiling at 69.0° at 760 mm. pressure was collected. Redistillation of this fraction showed no change in boiling point or composition. This fraction was analyzed by gas liquid chromatography and found to possess the following composition

	Percent
Tetrachlorodifluoroethane	76.8
Isopropanol	10.2
Nitromethane	9.3
Water	3.7

On standing, the fraction separated into two layers. The lower layer, which constituted 96.0% of the total fraction, was analyzed by gas liquid chromatography and was found to possess the following composition

	Percent
Tetrachlorodifluoroethane	80.0
Isopropanol	9.7
Nitromethane	9.3
Water	1.0

(b) Repetition of the procedure set out in Part (a), but substituting an equivalent amount of pure (97 mole percent) 1,1,2,2-tetrachloro-1,2-difluoroethane for the commercially available mixture of isomers gave a quaternary azeotrope boiling at 69.1° at 760 mm. pressure and having essentially the same composition as that mixture obtained by using the commercial mixture of tetrachlorodifluoroethane isomers.

(c) Repetition of the procedure set out in Part (a), above, but substituting an equivalent amount of 1,1,1,2-tetrachloro-2,2-difluoroethane for the commercial mixture of isomers gave a quaternary azeotrope boiling at 68.6° at 760 mm. pressure and having essentially the same composition.

These results indicate that azeotropic mixtures in accordance with our invention can be obtained using either pure isomers of tetrachlorodifluoroethane or any mixture thereof. Such azeotropes possess substantially identical

compositions and have no significant difference in properties.

Example 2.—Preparation of the Quaternary Azeotrope

(a) Equimolecular quantities of tetrachlorodifluoroethane (b.p. 92.8°), the commercially available mixture, secondary butanol (b.p. 98.8°), nitromethane (b.p. 101.2°) and water (b.p. 100°) were charged to a still equipped with a fractionating column. This mixture was heated to reflux and then distilled. The fraction boiling at 70.5° at 760 mm. pressure was collected. Redistillation of this fraction showed no change in boiling point or composition. This fraction was analyzed by gas liquid chromatography and found to possess the following composition

	Percent
Tetrachlorodifluoroethane	78.6
Sec.-Butanol	2.6
Nitromethane	14.1
Water	4.7

On standing, the fraction separated into two layers. The lower layer, which constituted 95.3% of the total fraction, was analyzed by gas liquid chromatography and was found to possess the following composition

	Percent
Tetrachlorodifluoroethane	89.36
Sec.-butanol	2.0
Nitromethane	8.6
Water	0.04

(b) Repetition of the procedure set out in Part (a), but substituting an equivalent amount of pure (97 mole percent) 1,1,2,2-tetrachloro-1,2-difluoroethane for the commercially available mixture of isomers gave a quaternary azeotrope boiling at 70.3° at 760 mm. pressure and having essentially the same composition as that mixture obtained by using the commercial mixture of tetrachlorodifluoroethane isomers.

(c) Repetition of the procedure set out in Part (a), above, but substituting an equivalent amount of 1,1,1,2-tetrachloro-2,2-difluoroethane for the commercial mixture of isomers gave a quaternary azeotrope boiling at 70.7° at 760 mm. pressure and having essentially the same composition.

These results indicate the azeotropic mixtures in accordance with our invention can be obtained using either pure isomers of tetrachlorodifluoroethane or any mixture thereof. Such azeotropes possess substantially identical compositions and have no significant difference in properties.

Example 3.—Use of the Quaternary Azeotrope as a Dry Cleaning Solvent for Leather

Swatches of natural (undyed) sheepskin suede leather, 2 in. x 8 in., were soiled with one of the following: lipstick, catsup, grape juice or lanolin. The stains were allowed to dry and to "set" for 24 hours at ambient temperature. The stained swatches were then cleaned in an agitated bath containing about 350 cc. of a particular test cleaning solvent.

The cleaning cycle was carried out for ½ hour and at ambient temperature.

The test solvents used were the azeotrope prepared in Example 1, Part (a) above, the respective components of the azeotrope, and perchloroethylene, a well known, commercially available dry cleaning solvent.

The results of these tests are set out in tabular form in Table 1 below. The effectiveness of the stain removal was rated by visual observation on a scale of 1 to 10 with 1 being substantially no stain removal and 10 being complete removal of the stain.

TABLE 1

Solvent	Stain			
	Lipstick	Grape juice	Catsup	Lanolin
$C_2Cl_4F_2$	6	5	3	10
CH_3NO_2	5	4	2	7
H_2O	1	9	10	5
C_3H_7OH	8	8	4	10
Azeotrope	10	10	10	10
Perchloroethylene	7	6	6	10

These results indicate the general overall effectiveness of the azeotrope composition as a soil remover from suede leather. Other solvents tested, while as good for removal of a particular soil, are ineffective with respect to removal of one or more of the other stains tested.

The data set out in Table 1 indicate the presence of synergism in the quaternary mixture of the invention. The numerical ratings are approximations of the percentage removal of the several stains, that is a rating of 5 is equivalent to about 50% removal of the stain. These percentages multiplied by the concentration of the particular solvent in the quaternary mixture give a quantitative indication of the amount of the stain which would be expected to be removed by the solvent in the mixture. The sum of these results in each instance is less than the analogous value (rating$\times$10) actually obtained with the quaternary mixture.

Thus a quantitative summation of the removal of lipstick stain by each of the four component solvents totals 61.5% whereas the quaternary mixture removed 100% of the stain.

The total grape juice removed would be expected to be 60.57%. Actually 100% of this stain was removed by the azeotrope.

The total catsup removed would be expected to be 39.74%. Actually, 100% of the stain was removed.

The total lanolin removed would be expected to be 96.7%. Actually 100% of the lanolin was removed by the quaternary azeotrope.

Accordingly, based on this method of calculation, the novel quaternary azeotrope of the invention exhibits a synergistic effect in the removal of both oil-soluble and water-soluble stains from leather.

Example 4.—Use of the Quaternary Azeotrope Containing Sec.-Butanol as a Dry Cleaning Solvent for Leather

In an analogous manner to that described in Example 3 above, the quaternary azeotrope containing secondary butanol prepared in Example 2, Part (a) above, was tested as a dry cleaning solvent for soiled suede leather. In this instance Stoddard solvent, a well known commercially available dry cleaning solvent, was used in place of perchloroethylene as a standard.

The results of these tests are set out in Table II below.

TABLE 2

Solvent	Stain			
	Lipstick	Grape juice	Catsup	Lanolin
$C_2Cl_4F_2$	6	5	3	10
CH_3NO_2	5	4	2	7
H_2O	1	9	10	5
C_4H_9OH	7	9	2	10
Azeotrope	10	9	9	10
Stoddard solvent	8	5	3	10

These results indicate the general overall effectiveness of the azeotrope composition as a soil remover from suede leather. Other solvents tested, while as good or slightly superior for removal of a particular soil, are ineffective with respect to removal of one or more of the other stains tested. Using the method of calculation described in Example 3 above the data of Table II can likewise be used to indicate the presence of synergism in the azeotropic mixture tested in this Example.

Thus a quantitative summation of the removal of lipstick stain by each of the four component solvents totals 56.54% whereas the quaternary mixture removed 100% of the stain.

The total grape juice removed would be expected to be 51.4%. Actually, 90% of this stain was removed by the azeotrope.

The total catsup removed would be expected to be 35.34%. Actually, 90% of the stain was removed.

The total lanolin removed would be expected to be 93.2%. Actually 100% of the lanolin was removed by the quaternary azeotrope.

Accordingly, based on this method of calculation, the novel quaternary azeotrope of the invention exhibits a synergistic effect in the removal of both oil-soluble and water-soluble stains from leather.

Example 5.—Dry Cleaning of Water Sensitive Textiles with Lower Layer of Azeotrope

Certain textile materials, such as wool are sensitive to excessive moisture in dry cleaning solvents. Such sensitivity is evidenced by shrinkage. Some moisture is desirable, however, for effective cleaning.

As has been indicated, the quaternary azeotropes on standing, separate into two phases, the lower of which contains only a minimum quantity of water. This amount, in the presence of the organic solvents does not cause shrinkage and/or wrinkling of textiles during the cleaning of said textiles. The avoidance of shrinkage serves to preserve the original character of the cleaned textile. The absence of wrinkles reduces or eliminates the need for pressing of the cleaned textile.

This property of the lower phase of the azeotrope is shown by the following comparative test wherein the effect of this mixture of solvents on wool and rayon textile material was compared with a standard dry cleaning composition. The standard consisted of perchloroethylene containing 1% of water and 1% of Aerosol OT (a synthetic detergent consisting essentially of the sodium salt of dioctylsulfosuccinic acid).

In this test, measured swatches of the particular textile material were immersed in an agitated bath of the dry cleaning solvent composition for ½ hour at ambient temperature. After removal from the bath, the swatches were dried and remeasured for shrinkage. The samples, after cleaning, were checked for the presence of wrinkles.

The results of these tests are recorded in Table III below:

TABLE III

Solvent	Fabric	Original dimensions	Final dimensions	Appearance
Azeotrope of Ex. 1 Part a	Wool	5⅛" x 7"	5¼" x 6¾"*	Considerable wrinkling.
	Rayon	6" x 7"	No change	Do.
Lower layer containing isopropanol	Wool	6" x 7"	do	Smooth.
Lower layer containing sec. butanol	Wool	5¾" x 7"	do	Do.
	Rayon	6" x 7"	do	Do.
Perclene**	Wool	5¾" x 7"	do	Slight wrinkling.
	Rayon	6" x 7"	do	Do.

*Average shrinkage of 10%.
**Perchloroethylene containing 1% water and 1% Aerosol OT.

The used "lower layer" solvent mixture can be readily recovered by passing the solvent through a filter to remove solid particles. To the filtrate a mixture of about 4% water, 0.3% sec.-butanol and 0.8% nitromethane or a mixture of about 4% water, 0.88% isopropanol and 0.35% nitromethane is added and the mass is fed to a still. On distillation, a quaternary azeotrope of the same composition as that obtained in Example 2, Part (a) above or Example 1 Part (a), above is obtained. This is permitted to stratify and the lower layer is drawn off to a suitable storage vessel to be recycled. The upper layer of the azeotrope can be preserved for use as build up for used solvent in this recovery process. The still bottoms, consisting essentially of water and disolved soil, are discarded.

The novel solvent mixtures of the invention find other solvent applicants such as for removing gases, oils and inorganic salts from a variety of industrial items, for cleaning of photographic films and prints, for removal of buffing compounds, such as rouge, and also may be used as heat exchange media and as chemical reaction media.

It will be apparent to those skilled in the art that, for specialized purposes, various additives could be incorporated with the novel mixtures of the invention, for example lubricants, water proofing resins, moth proofing chemicals and the like. These additives are chosen and used in amounts so as not to adversely affect the essential properties of the mixtures for a given purpose.

The invention is not intended to be limited by any specific embodiments disclosed herein, but only by the scope of the following claims.

We claim:

1. A solvent mixture suitable for use as a dry cleaning solvent for textile materials consisting essentially of about 80.0 weight percent of tetrachlorodifluoroethane, about 9.7 weight percent of isopropanol, about 9.3 weight percent of nitromethane and about 1.0 weight percent of water.

2. A solvent mixture suitable for use as a dry cleaning solvent for textile materials consisting essentially of about 89.36 weight percent of tetrachlorodifluoroethane, about 2.0 weight percent of secondary butanol, about 8.6 weight percent of nitromethane and about 0.04 weight percent of water.

3. The process of dry cleaning textile materials susceptible to shrinkage and wrinkling by aqueous agents which comprises contacting for a period of time sufficient to effect substantially complete dissolution of oil-soluble and water-soluble stains, such textile materials with a solvent mixture as described in claim **1**, separating said materials from said solvent mixture and drying said material.

4. The process of dry cleaning textile materials susceptible to shrinkage and wrinkling by aqueous agents which comprises contacting for a period of time sufficient to effect substantially complete dissolution of oil-soluble and water-soluble stains, such textile materials with a solvent mixture as described in claim **2**, separating said materials from said solvent mixture and drying said material.

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U.S. Cl. X.R.

8—142; 252—DIG. 9