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TERTIARY AZEOTROPIC CLEANING SOLUTION BASED ON TETRACHLORODIFLUOROETHANE

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ABSTRACT OF THE DISCLOSURE

A ternary azeotrope of tetrachlorodifluoroethane, dichloroethane and methanol has superior properties for solvent vapor cleaning and degreasing applications.

This application is a division of our copending U.S. application Ser. No. 771,334 filed Oct. 28, 1968 and now U.S. Pat. 3,640,884.

This invention relates to binary and ternary azeotropic mixtures of tetrachlorodifluoroethane. The binary azeotropes contain tetrachlorodifluoroethane as one component and either acetic acid, propionic acid, dioxane, monomethyl ether of ethylene glycol, ethyl acetate, isopropyl acetate or n-propyl acetate as the second component. The ternary azeotropes contain tetrachlorodifluoroethane as the first component, 1,2-dichloroethane as the second component and either methanol, ethanol or isopropanol as the third component. It has been discovered that these azeotropes may be used in solvent vapor cleaning and degreasing applications.

Chlorofluoroethane solvents known in the art ordinarily do not have sufficient solvent power to clean "printed circuit boards;" that is, to effectively remove the rosin flux and other contaminants deposited on the surface of such boards during the application of conductive metal leads thereto. Ultrasonic or vapor degreasing techniques may be used to improve the cleaning action of such solvents. Although mixtures of solvents have been used for this purpose they have the disadvantage that they boil over a range of temperatures and consequently undergo fractionation in vapor degreasing or ultrasonic applications which are open to the atmosphere. Additionally, when employing either of these methods the solvent must also be relatively nontoxic and nonflammable for safety reasons.

Tetrachlorodifluoroethane is a relatively high boiling fluorocarbon and for this reason especially advantageous in vapor degreasing applications. At these temperatures the vapor has more of a tendency to dissolve high melting greases, or fluxed as well as oil residues and the like and at a faster rate. When articles such as circuit boards are passed through a vapor degreaser, the solvent vapors tend to condense on the article until the articles are heated by the vapors from room temperature to the temperature of the vapor. The condensation thus formed on the articles tends to drip back into the solvent reservoir taking with it some of the soil on the article. For this reason the ability of a cleaning solvent to condense on and wet the surface is especially advantageous. Higher boiling solvents prolong this condensation effect in a continuous degreaser since it takes a greater amount of time to bring the article passing through the degreaser up to the vapor temperature of the solvent. Consequently higher boiling solvents generally allow for longer periods of cleaning action per unit of time in a continuous vapor degreaser than the lower boiling solvents.

Tetrachlorodifluoroethane also is a better solvent for most types of materials than trichlorotrifluoroethane however, it suffers the disadvantage that it is solidus at room temperature whereas the latter is liquidus. Accordingly tetrachlorodifluoroethane is more difficult to handle than liquid type cleaning solvents.

It is an object of this invention to provide a constant boiling or azeotropic solvent that is a liquid at room temperature, will not fractionate and also has the foregoing advantages. Another object is to provide an azeotropic composition which is valuable as a solvent for oils and greases and particularly for cleaning printed circuits. A further object is to provide an azeotropic composition which is both relatively nontoxic and nonflammable both in the liquid phase and in the vapor phase and which at the same time is an excellent solvent for cleaning printed circuits especially by continuous vapor degreasing or ultrasonic means.

The above object of this invention may be accomplished by novel mixtures comprising a two component composition of tetrachlorodifluoroethane (e.g. 1,1,2,2-tetrachloro-1,2-difluoroethane) as a first component and either acetic acid, propionic acid, dioxane, monomethyl ether of ethylene glycol, ethyl acetate, ispropyl acetate or n-propyl acetate as a second component. The above objects of this invention may also be accomplished by novel mixtures comprising a three component composition of tetrachlorodifluoroethane (e.g. 1,1,2,2 - tetrachloro - 1,2 - difluoroethane) as a first component, 1,2-dichloroethane as a second component and either methanol, ethanol or isopropanol as a third component.

Although 1,1,2,2 - tetrachloro - 1,2 - difluoroethane is a preferred tetrachlorodifluoroethane component, the isomer 1,1,1,2 - tetrachloro - 2,2 - difluoroethane may be substituted as a component therefore in whole or in part and especially in minor amounts or trace amounts. All of these aforementioned mixtures form azeotropes which distill at a constant temperature, the liquid phase and the vapor phase in equilibrium therewith having the same composition. Such mixtures are relatively nontoxic in both the liquid phase and the vapor phase. These mixtures are particularly useful as solvents for greases, oils, waxes and the like and are particularly useful for cleaning printed circuits.

Although the aforementioned azeotropic mixtures are obtained at approximately 760 mm. Hg a variation in pressure and consequently a change in the compositions and boiling points are also intended to be within the broad scope of the invention. Thus the azeotropes may contain many different proportions of the aforementioned components provided a constant boiling mixture is obtained at the various pressures at which the compositions are used. Stated otherwise any pressure may be employed to obtain the azeotropes of this invention as long as a two component or three component constant boiling mixture is obtained, and accordingly the ratio of components of the azeotropes of the invention will also vary. The variation of components is thus within the skill of the art and is thus within the skill of the art and is easily determined once it is known that the organic compounds of this invention will form the aforementioned azeotropes. In a preferred embodiment the present invention relates to the aforementioned azeotropes that boil at atmospheric pressure ± about 25, especially about ± 15 mm. Hg pressure.

EXAMPLE 1

An azeotropic composition is obtained by distilling a mixture of 1,1,2,2-tetrachloro-1,2-difluoroethane and acetic acid. The mixture is charged to a laboratory scale distillation flask having an overhead condenser with provision for the removal of the distillate. The mixture is heated to its atmospheric boiling point and distilled at a high reflux. An azeotropic mixture is obtained consisting

essentially of about 93.0 parts 1,1,2,2-tetrachloro-1,2-difluoroethane and about 7.0 parts acetic acid on a weight basis, based on refractive index analysis, the boiling point of which is about 194.3° F. measured at substantially 760 millimeters Hg pressure.

EXAMPLES 2–10

The process of Example 1 is repeated using the components noted in Table I and the composition is measured by gas chromatographic analysis and the boiling points of each azeotrope is measured as in Table I.

TABLE I

Ex. No.	Binary azeotropes components	Composition (percent by weight)	Normal boiling point,[1] ° F.
1	1,1,2,2-tetrachloro-1,2-difluoroethane acetic acid.	93.0–7.0	194.3
2	1,1,2,2-tetrachloro-1,2-difluoroethane propionic acid.	>95–<5	199.3
3	1,1,2,2-tetrachloro-1,2-difluoroethane dioxane.	88.0–12.0	197.3
4	1,1,2,2-tetrachloro-1,2-difluoroethane monomethyl ether of ethylene glycol.	91.8–8.2	197
5	1,1,2,2-tetrachloro-1,2-difluoroethane ethyl acetate.	7.2–92.8	.172.1
6	1,1,2,2-tetrachloro-1,2-difluoroethane isopropyl acetate.	23.7–76.3	192.0
7	1,1,2,2-tetrachloro-1,2-difluoroethane n-propyl acetate.	9.4–90.6	197.0
	Ternary azeotropes		
8	1,1,2,2-tetrachloro-1,2-difluoroethane 1,2-dichloroethane methanol.	55.0–17.0–28.0	138.3
9	1,1,2,2-tetrachloro-1,2-difluoroethane 1,2-dichloroethane ethanol.	44.0–33.0–23.0	158.5
10	1,1,2,2-tetrachloro-1,2-difluoroethane 1,2-dichloroethane isopropanol.	37.0–38.0–25.0	165.4

[1] ~760 mm. Hg pressure.

A printed circuit board coated with a rosin flux is cleaned in an ultrasonic degreasing apparatus with the azeotropic mixtures of this invention and substantially all of the rosin flux is removed without any observable detrimental effect on the board which constitutes the backing of the printed circuit.

The formation of the azeotropes of this invention is unexpected in view of the fact that azeotropes could not be obtained with the following binary and ternary systems of tetrachlorodifluoroethane listed in Table II:

TABLE II.—SYSTEMS WHICH DID NOT FORM AZEOTROPES

(1) Binary

Components:

1,1,2,2-tetrachloro-1,2-difluoroethane/acetone
1,1,2,2-tetrachloro-1,2-difluoroethane/benzene
1,1,2,2-tetrachloro-1,2-difluoroethane/chloroform
1,1,2,2-tetrachloro-1,2-difluoroethane/cyclohexane
1,1,2,2-tetrachloro-1,2-difluoroethane/1,1-dichloroethane
1,1,2,2-tetrachloro-1,2-difluoroethane/heptane
1,1,2,2-tetrachloro-1,2-difluoroethane/methylene chloride
1,1,2,2-tetrachloro-1,2-difluoroethane/perchloroethylene
1,1,2,2-tetrachloro-1,2-difluoroethane/toluene
1,1,2,2-tetrachloro-1,2-difluoroethane/1,1,1-trichloroethane

(2) Ternary

1,1,2,2-tetrachloro-1,2-difluoroethane/methanol/water
1,1,2,2-tetrachloro-1,2-difluoroethane/perchloroethylene/methanol
1,1,2,2-tetrachloro-1,2-difluoroethane/perchloroethylene/ethanol
1,1,2,2-tetrachloro-1,2-difluoroethane/perchloroethylene/isopropanol

Because of the fluctuation in ambient pressures as discussed previously, the compositions of the azeotrope components as well as their equivalents noted herein will also vary as in Table III.

In the following claims it is intended that the components contained therein as well as those of Table III herein and their disclosed and art known equivalents, be construed in such a manner so that for example 1,1,2,2-tetrachloro-1,2-difluoroethane in an amount of about 93 parts ± about 10% shall mean about 83.7 parts to about 102.3 parts on a weight basis and likewise for the other components noted in Table III and the claims as well as their equivalents, especially those equivalents noted herein.

Although the invention has been described by reference to some preferred embodiments it is not intended that the broad scope of the novel azeotropic compositions be limited thereby but that certain modifications are intended to be included within the spirit and broad scope of the following claims.

TABLE III

Components	Binary azeotrospes	Composition, parts by weight
1,1,2,2-tetrachloro-1,2-difluoroethane		About 93 parts ± about 10% especially ± about 5%.
Do	Acetic acid	About 7 parts ± about 10% especially ± about 5%.
Do		About 95 parts ± about 10% especially ± about 5%.
Do	Propionic acid	About 5 parts ± about 10% especially ± about 5%.
Do		About 88 parts ± about 10% especially ± about 5%.
Do	Dioxane	About 12 parts ± about 10% especially ± about 5%.
Do		About 91.8 parts ± about 10% especially ± about 5%.
Do	Monomethyl ether of ethylene glycol	About 8.2 parts ± about 10% especially ± about 5%.
Do		About 7.2 parts ± about 10% especially ± about 5%.
Do	Ethyl acetate	About 92.8 parts ± about 10% especially ± about 5%.
Do		About 23.7 parts ± about 10% especially ± about 5%.
Do	Isopropyl acetate	About 76.3 parts ± about 10% especially ± about 5%.
Do		About 9.4 parts ± about 10% especially ± about 5%.
Do	n-Propyl acetate	About 90.6 parts ± about 10% especially ± about 5%.
	Ternary azeotropes	
Do		About 55.0 parts ± about 10% especially ± about 5%.
Do	1,2-dichloroethane	About 17.0 parts ± about 10% especially ± about 5%.
Do	Methanol	About 28.0 parts ± about 10% especially ± about 5%.
Do		About 44 parts ± about 10% especially ± about 5%.
Do	1,2-dichloroethane	About 33 parts ± about 10% especially ± about 5%.
Do	Ethanol	About 23 parts ± about 10% especially ± about 5%.
Do		About 37 parts ± abotu 10% especially ± about 5%.
Do	1,2-dichloroethane	About 38 parts ± about 10% especially ± about 5%.
Do	Isopropanol	About 25 parts ± about 10% especially ± about 5%.

What is claimed is:

1. A composition of matter consisting essentially of an azeotrope which at about 760 millimeters of mercury pres-

sure and at about 138° F. consists essentially of about 55 percent by weight 1,1,2,2-tetrachloro-1,2-difluoroethane, about 17 percent by weight 1,2-dichloroethane and about 28 percent by weight of methanol.

2. A method for cleaning a surface by contacting said surface with a composition of matter consisting essentially of an azeotrope which at about 760 millimeters of mercury pressure and at about 138° F. consists essentially of about 55 percent by weight 1,1,2,2-tetrachloro-1,2-difluoroethane, about 17 percent by weight 1,2-dichloroethane and about 28 percent by weight of methanol.

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