(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 421 730 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **90310776.1**

(51) Int. Cl.[5]: **C23G 5/028**, C11D 7/50

(22) Date of filing: **02.10.90**

(30) Priority: **04.10.89 US 417655**

(43) Date of publication of application:
10.04.91 Bulletin 91/15

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(71) Applicant: **E.I. DU PONT DE NEMOURS AND COMPANY**
1007 Market Street
Wilmington Delaware 19898(US)

(72) Inventor: **Merchant, Abid Nazarali**
1408 Clive Circle
Wilmington, Delaware 19803(US)

(74) Representative: **Woodcraft, David Charles et al**
BROOKES & MARTIN High Holborn House
52/54 High Holborn
London, WC1V 6SE(GB)

(54) Ternary azeotropic compositions of 1,1-dichloro-1,2-difluoroethane and trans-1,2-dichloroethylene with methanol, ethanol or isopropanol.

(57) Azeotropic mixtures of 1,1-dichloro-1,2-difluoroethane (HCFC-132c) with trans-1,2-dichloroethylene (T-CFC-1130) and methanol or ethanol or isopropanol, the azeotropic mixtures being useful in solvent cleaning applications.

EP 0 421 730 A2

TERNARY AZEOTROPIC COMPOSITIONS OF 1,1-DICHLORO-1,2-DIFLUOROETHANE AND TRANS-1,2-DICHLOROETHYLENE WITH METHANOL, ETHANOL OR ISOPROPANOL

INVENTION BACKGROUND

As modern electronic circuit boards evolve toward increased circuit and component densities, thorough board cleaning after soldering becomes a more important criterion. Current industrial processes for soldering electronic components to circuit boards involve coating the entire circuit side of the board with flux and thereafter passing the flux-coated board over preheaters and through molten solder. The flux cleans the conductive metal parts and promotes solder fusion. Commonly used solder fluxes generally consist of rosin, either used alone or with activating additives, such as amine hydrochlorides or oxalic acid derivatives.

After soldering, which thermally degrades part of the rosin, the flux-residues are often removed from the circuit boards with an organic solvent. The requirements for such solvents are very stringent. Defluxing solvents should have the following characteristics: a low boiling point, be nonflammable, have low toxicity and have high solvency power, so that flux and flux-residues can be removed without damaging the substrate being cleaned.

While boiling point, flammability and solvent power characteristics can often be adjusted by preparing solvent mixtures, these mixtures are often unsatisfactory because they fractionate to an undesirable degree during use. Such solvent mixtures also fractionate during solvent distillation, which makes it virtually impossible to recover a solvent mixture with the original composition.

On the other hand, azeotropic mixtures, with their constant boiling points and constant compositions, have been found to be very useful for these applications. Azeotropic mixtures exhibit either a maximum or minimum boiling point and they do not fractionate on boiling. These characteristics are also important when using solvent compositions to remove solder fluxes and flux-residues from printed circuit boards. Preferential evaporation of the more volatile solvent mixture components would occur, if the mixtures were not azeotropic and would result in mixtures with changed compositions, and with less-desirable solvency properties, such as lower rosin flux solvency and lower inertness toward the electrical components being cleaned. The azeotropic character is also desirable in vapor degreasing operations, where redistilled solvent is generally employed for final rinse cleaning.

In summary, vapor defluxing and degreasing systems act as a still. Unless the solvent composition exhibits a constant boiling point, i.e., is a single material, or is an azeotrope, fractionation will occur and undesirable solvent distributions will result, which could detrimentally affect the safety and efficacy of the cleaning operation.

A number of halocarbon based azeotropic compositions have been discovered and in some cases used as solvents for solder flux and flux-residue removal from printed circuit boards and also for miscellaneous degreasing applications. For example: U.S. Patent No, 3,903,009 discloses the ternary azeotrope of 1,1,2-trichloro-1,2,2-trifluoroethane with ethanol and nitromethane; U.S. Patent No. 2,999,815 discloses the binary azeotrope of 1,1,2-trichloro-1,2,2-trifluoroethane and acetone. U.S. Patent No. 2,999,816 discloses the binary azeotrope of 1,1,2-trichloro-1,2,2-trifluoroethane and methyl alcohol. U.S. Patent No. 4,767,561 discloses the ternary azeotrope of 1,1,2-trichloro-1,2,2-trifluoroethane, methanol and 1,2-dichloroethylene.

Some of the chlorofluorocarbons which are currently used for cleaning and other applications have been theoretically linked to depletion of the earth,s ozone layer. As early as the mid-1970,s, it was known that introduction of hydrogen into the chemical structure of previously fully-halogenated chlorofluorocarbons reduced the chemical stability of these compounds. Hence, these now destabilized compounds would be expected to degrade in the lower atmosphere and not reach the stratospheric ozone layer in-tact. What is also needed, therefore, are substitute chlorofluorocarbons which have low theoretical ozone depletion potentials.

Unfortunately, as recognized in the art, it is not possible to predict the formation of azeotropes. This fact obviously complicates the search for new azeotropic compositions, which have application in the field. Nevertheless, there is a constant effort in the art to discover new azeotropic compositions, which have desirable solvency characteristics and particularly greater versatilities in solvency power.

SUMMARY OF THE INVENTION

According to the present invention, azeotropic compositions have been discovered comprising admixtures of effective amounts of 1,1-dichloro-1,2-difluoroethane with trans-1,2-dichloroethylene plus an alcohol from the group consisting of methanol, ethanol and isopropanol.

More specifically, the azeotropic mixtures are: an admixture of about 51-61 weight percent 1,1-dichloro-1,2-difluoroethane and about 31-41 weight percent trans-1,2-dichloroethylene and about 4-10 weight percent methanol; an admixture of about 65-75 weight percent 1,1-dichloro-1,2-difluoroethane and about 19-29 weight percent trans-1,2-dichloroethylene and about 3-7 weight percent ethanol; an admixture of about 61-71 weight percent 1,1-dichloro-1,2-difluoroethane and about 27-37 weight percent trans-1,2-dichloroethylene and about 0.7-1.7 weight percent isopropanol.

The present invention provides nonflammable azeotropic compositions which are well suited for solvent cleaning applications.

DETAILED DESCRIPTION

The compositions of the instant invention comprise admixtures of effective amounts of 1,1-dichloro-1,2-difluoroethane ($CFCl_2CH_2F$, boiling point = 48.4° C) with trans-1,2-dichloroethylene (boiling point = 48° C) and an alcohol selected from the group consisting of methanol (CH_3OH, boiling point = 64.6° C) or ethanol (CH_3CH_2OH, boiling point = 78° C) or isopropanol ($CH_3CHOHCH_3$, boiling point = 82° C) to form azeotropic compositions. The halogenated materials are known as HCFC-132c and T-HCC-1130, respectively, in the nomenclature conventional to the halocarbon field.

By azeotropic composition is meant, a constant boiling liquid admixture of three or more substances, whose admixture behaves as a single substance, in that the vapor, produced by partial evaporation or distillation of the liquid has substantially the same composition as the liquid, i.e., the admixture distills without substantial compositional change. Constant boiling compositions, which are characterized as azeotropic, exhibit either a maximum or minimum boiling point, as compared with that of the nonazeotropic mixtures of the same substances.

For purposes of this invention, effective amount is defined as the amount of each component of the instant invention admixture which, when combined, results in the formation of the azeotropic compositions of the instant invention. This definition includes the amounts of each component, which amounts may vary depending upon the pressure applied to the composition so long as the azeotropic compositions continue to exist at the different pressures, but with possible different boiling points. Therefore, effective amount includes each components, weight percentage for each composition of the instant invention, which form azeotropic compositions at pressures other than atmospheric pressure.

The language "an azeotropic composition consisting essentially of..." is not intended to exclude the inclusion of minor amounts of other materials which do not significantly alter the azeotropic character of the composition.

It is possible to characterize, in effect, a constant boiling admixture, which ray appear under many guises, depending upon the corditions chosen, by any of several criteria:

* The composition can be defined as an azeotrope of A, B, and C since the very term "azeotrope" is at once both definitive and limitative, and requires that effective amounts of A, B and C form this unique composition of matter, which is a constant boiling admixture.

* It is well known by those skilled in the art that at different pressures, the composition of a given azeotrope will vary - at least to some degree - and changes in pressure will also change - at least to some degree - the boiling point temperature. Thus an azeotrope of A, B and C represents a unique type of relationship but with a variable composition which depends on temperature and/or pressure. Therefore compositional ranges, rather than fixed compositions, are often used to define azeotropes.

* The composition can be defined as a particular weight percent relationship or mole percent relationship of A, B and C, while recognizing that such specific values point out only one particular such relationship and that in actuality, a series of such relationships, represented by A, B and C actually exist for a given azeotrope, varied by the influence of pressure.

* Azeotrope A, B and C can be characterized by defining the composition as an azeotrope characterized by a boiling point at a given pressure, thus giving identifying characteristics without unduly limiting the scope of the invention by a specific numerical composition, which is limited by and is only as accurate as the analytical equipment available.

Ternary mixtures of about 51-61 weight percent 1,1-dichloro-1,2-difluoroethane and about 31-41 weight percent trans-1,2-dichloroethylene and about 4-10 weight percent methanol are characterized as azeotropic,

in that mixtures within this range exhibit a substantially constant boiling point at constant pressure. Being substantially constant boiling, the mixtures do not tend to fractionate to any great extent upon evaporation. After evaporation, only a small difference exists between the composition of the vapor and the composition of the initial liquid phase. This difference is such that the compositions of the vapor and liquid phases are considered substantially identical. Accordingly, any mixture within this range exhibits properties which are characteristic of a true ternary azeotrope. The ternary composition consisting of about 56.5 weight percent 1,1-dichloro-1,2-difluoroethane, about 36.5 weight percent trans-1,2-dichloroethylene and about 7.0 weight percent methanol has been established, within the accuracy of the fractional distillation method, as a true ternary azeotrope, boiling at about 41.0 ° C, at substantially atmospheric pressure.

Also, according to the instant invention, ternary mixtures of about 65-75 weight percent 1,1-dichloro-1,2-difluoroethane, about 19-29 weight percent trans-1,2-dichloroethylene and about 3-7 weight percent ethanol are characterized as azeotropic, in that mixtures within this range exhibit a substantially constant boiling point at constant pressure. Being substantially constant boiling, the mixtures do not tend to fractionate to any great extent upon evaporation. After evaporation, only a small difference exists between the composition of the vapor and the composition of the initial liquid phase. This difference is such that the compositions of the vapor and liquid phases are considered substantially identical. Accordingly, any mixture within this range exhibits properties which are characteristic of a true ternary azeotrope. The ternary composition consisting of about 70.0 weight percent 1,1-dichloro-1,2-difluoroethane, about 24.6 weight percent trans-1,2-dichloroethylene and about 5.4 weight percent ethanol has been established, within the accuracy of the fractional distillation method, as a true ternary azeotrope, boiling at about 44.5 ° C, at substantially atmospheric pressure.

Also, according to the instant invention, ternary mixtures of about 61-71 weight percent 1,1-dichloro-1,2-difluoroethane, about 27-37 weight percent trans-1,2-dichloroethylene and about 0.7-1.7 weight percent isopropanol are characterized as azeotropic, in that mixtures within this range exhibit a substantially constant boiling point at constant pressure. Being substantially constant boiling, the mixtures do not tend to fractionate to any great extent upon evaporation. After evaporation, only a small difference exists between the composition of the vapor and the composition of the initial liquid phase. This difference is such that the compositions of the vapor and liquid phases are considered substantially identical. Accordingly, any mixture within this range exhibits properties which are characteristic of a true ternary azeotrope. The ternary composition consisting of about 66.3 weight percent 1,1-dichloro-1,2-difluoroethane, about 32.5 weight percent trans-1,2-dichloroethylene and about 1.2 weight percent isopropanol has been established, within the accuracy of the fractional distillation method, as a true ternary azeotrope, boiling at about 46.5 ° C, at substantially atmospheric pressure.

The aforestated azeotropes have low ozone-depletion potentials and are expected to decompose almost completely, prior to reaching the stratosphere.

The azeotropic compositions of the present invention permit easy recovery and reuse of the solvent from vapor defluxing and decreasing operations because of their azeotropic nature. As an example, the azeotropic mixtures of this invention can be used in cleaning processes such as described in U.S. Patent No. 3,881,949, which is incorporated herein by reference.

The azeotropic compositions of the instant invention can be prepared by any convenient method including mixing or combining the desired component amounts. A preferred method is to weigh the desired component amounts and thereafter combine them in an appropriate container.

EXAMPLES

Example 1

A solution which contained 61.7 weight percent 1,1-dichloro-1,2-difluoroethane, 31.8 weight percent trans-1,2-dichloroethylene and 6.5 weight percent methanol was prepared in a suitable container and mixed thoroughly.

The solution was distilled in a Perkin-Elmer Model 251 autoannular spinning band still (200 plate fractionating capability), using about a 10:1 reflux to take-off ratio. Head temperatures were read directly to 0.1 ° C. All temperatures were adjusted to 760 mm pressure. Distillate compositions were determined by gas chromatography. Results obtained are summarized in Table 1.

TABLE 1

DISTILLATION OF: (61.7 + 31.8 + 6.5)					
1,1-DICHLORO-1,2-DIFLUOROETHANE (DCDFE), TRANS-1,2-DICHLOROETHYLENE (T-DCE) AND METHANOL (MEOH)					
CUTS	TEMPERATURE, °C POT	WT.% DISTILLED OR RECOVERED	DCDFE	T-DCE	MEOH
1	41.1	2.6	57.1	35.7	7.2
2	41.0	10.3	56.1	36.9	7.0
3	41.1	15.0	56.1	36.8	7.1
4	41.1	20.0	56.5	36.5	7.0
5	41.1	22.0	56.6	36.4	7.0
6	41.1	25.0	56.8	36.3	6.9
7	41.1	30.0	56.9	36.2	6.9
HEEL	--	79.8	63.4	29.5	7.1

Analysis of the above data indicates very small differences among head temperatures and distillate compositions, as the distillation progressed. A statistical analysis of the data indicates that the true ternary azeotrope of 1,1-dichloro-1,2-difluoroethane, trans-1,2-dichloroethylene and methanol has the following characteristics at atmospheric pressure (99 percent confidence limits):

1,1-Dichloro-1,2-difluoroethane = 56.5 ± 1.3 wt.%

trans-1,2-Dichloroethylene = 36.5 ± 1.1 wt.%

Methanol = 7.0 ± 0.3 wt.%

Boiling point, °C = 41.0 ± 0.1

Example 2

A solution which contained 76.3 weight percent 1,1-dichloro-1,2-difluoroethane, 16.8 weight percent trans-1,2-dichloroethylene 6.9 weight percent ethanol was prepared in a suitable container and mixed thoroughly.

The solution was distilled in a Perkin-Elmer Model 251 autoannular spinning band still (200 plate fractionating capability), using about a 10:1 reflux to take-off ratio. Head temperatures were read directly to 0.1 °C. All temperatures were adjusted to 760 mm pressure. Distillate compositions were determined by gas chromatography. Results obtained are summarized in Table 2.

TABLE 2

DISTILLATION OF: (76.3 + 16.8 + 6.9)					
1,1-DICHLORO-1,2-DIFLUOROETHANE (DCDFE), TRANS-1,2-DICHLOROETHYLENE (T-DCE) AND ETHANOL (ETOH)					
CUTS	TEMPERATURE, °C HEAD	WT.% DISTILLED OR RECOVERED	DCDFE	T-DCE	ETOH
1	44.5	5.0	70.0	24.6	5.4
2	44.5	9.8	69.6	25.0	5.4
3	44.5	14.6	69.8	24.9	5.3
4.	44.5	20.0	69.7	24.8	5.5
5	44.5	24.4	70.2	24.5	5.3
6	44.5	28.6	70.8	23.8	5.4
7	50.0	32.9	72.4	22.4	5.2
HEEL	--	93.5	86.2	5.6	8.2

Analysis of the above data indicates very small differences among head temperatures and distillate compositions, as the distillation progressed. A statistical analysis of the data indicates that the true ternary azeotrope of 1,1-dichloro-1,2-difluoroethane, trans-1,2-dichloroethylene and ethanol has the following characteristics at atmospheric pressure (99 percent confidence limits):
1,1-Dichloro-1,2-difluoroethane = 70.0 ± 1.9 wt.%
trans-1,2-Dichloroethylene = 24.6 ± 1.9 wt.%
Ethanol = 5.4 ± 0.3 wt.%
Boiling point, °C = 44.5 ± 0.1

Example 3

A solution which contained 64.6 weight percent 1,1-dichloro-1,2-difluoroethane, 30.0 weight percent trans-1,2-dichloroethylene and 5.4 weight percent isopropanol was prepared in a suitable container and mixed thoroughly.

The solution was distilled in a Perkin-Elmer Model 251 autoannular spinning band still (200 plate fractionating capability), using about a 10:1 reflux to take-off ratio. Head temperatures were read directly to 0.1 °C. All temperatures were adjusted to 760 mm pressure. Distillate compositions were determined by gas chromatography. Results obtained are summarized in Table 3.

TABLE 3

DISTILLATION OF: (64.6 + 30.0 + 5.4)					
1,1-DICHLORO-1,2-DIFLUOROETHANE (DCDFE), TRANS-1,2-DICHLOROETHYLENE (T-DCE) AND ISOPROPANOL(IPROH)					
CUTS	TEMPERATURE, °C HEAD	WT.% DISTILLED OR RECOVERED	DCPFP	T-DCE	IPROH
1	45.9	14.7	64.6	34.4	1.0
2	46.4	29.8	65.8	32.9	1.3
3	46.4	41.6	65.9	32.9	1.2
4	46.3	65.2	66.8	31.9	1.3
5	46.7	72.8	66.5	32.4	1.1
6	46.9	87.6	69.3	29.3	1.4
HEEL		100.0	63.8	12.4	23.8

Analysis of the above data indicates very small differences among head temperatures and distillate compositions, as the distillation progressed. A statistical analysis of the data indicates that the true ternary azeotrope of 1,1-dichloro-1,2-difluoroethane, trans-1,2-dichloroethylene and isopropanol has the following characteristics at atmospheric pressure (99 percent confidence limits):
1,1-Dichloro-1,2-difluoroethane = 66.3 ± 2.2 wt.%
trans-1,2-Dichloroethylene = 32.5 ± 2.2 wt.%
Isopropanol = 1.2 ± 0.3 wt.%
Boiling point, °C = 46.5 ± 0.8

Example 4

Several single sided circuit boards were coated with activated rosin flux and soldered by passing the board over a preheater to obtain a top side board temperature of approximately 200 °F (93 °C) and then through 500 °F (260 °C) molten solder. The soldered boards were defluxed separately with the three azeotropic mixtures cited in Examples 1, 2 and 3 above, by suspending a circuit board, first, for three minutes in the boiling sump, which contained the azeotropic mixture, then, for one minute in the rinse sump, which contained the same azeotropic mixture, and finally, for one minute in the solvent vapor above the boiling sump. The boards cleaned in each azeotropic mixture had no visible residue remaining thereon.

Claims

1. An azeotropic composition comprising effective amounts of: 1,1-dichloro-1,2-difluoroethane with trans-1,2-dichloroethylene plus an alcohol selected from the group consisting of methanol, ethanol and isopropanol.

2. The azeotropic composition of Claim 1, consisting essentially of about 51-61 weight percent 1,1-dichloro-1,2-difluoroethane, about 31-41 weight percent trans-1,2-dichloroethylene, and about 4-10 weight percent methanol.

3. The azeotropic composition of Claim 1, consisting essentially of about 65-75 weight percent 1,1-dichloro-1,2-difluoroethane and about 19-29 weight percent trans-1,2-dichloroethylene and about 3-7 weight percent ethanol.

4. The azeotropic composition of Claim 1, consisting essentially of about 61-71 weight percent 1,1-dichloro-1,2-difluoroethane, and about 27-37 weight percent trans-1,2-dichloroethylene and about 0.7-1.7 weight percent isopropanol.

5. The azeotropic composition of Claim 2, consisting essentially of about 56.5 weight percent 1,1-dichloro-1,2-difluoroethane, and about 36.5 weight percent trans-1,2-dichloroethylene and about 7.0 weight percent methanol.

6. The azeotropic composition of Claim 2, wherein the composition has a boiling point of about 41.0 $^{\circ}$ C at substantially atmospheric pressure.

7. The azeotropic composition of Claim 3, consisting essentially of about 70.0 weight percent 1,1-dichloro-1,2-difluoroethane, and about 24.6 weight percent trans-1,2-dichloroethylene and about 5.4 weight percent ethanol.

8. The azeotropic composition of Claim 3, wherein the composition has a boiling point of about 44.5 $^{\circ}$ C, at substantially atmospheric pressure.

9. The azeotropic composition of Claim 4, consisting essentially of about 66.3 weight percent 1,1-dichloro-1,2-difluoroethane and about 32.5 weight percent trans-1,2-dichloroethylene and about 1.2 weight percent isopropanol.

10. The azeotropic composition of Claim 4, wherein the composition has a boiling point of about 46.5 $^{\circ}$ C, at substantially atmospheric pressure.

11. A process for cleaning a solid surface which comprises treating said surface with the azeotropic composition of Claim 1.

12. The process of Claim 11, wherein the solid surface is a printed circuit board contaminated with flux and flux-residues.

13. The process of Claim 12, wherein the solid surface is a metal.