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Schofield et al.

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[54] AZEOTROPIC COMPOSITION

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[52] **U.S. Cl.** **252/171,** 252/66, 252/DIG. 9

[51] **Int. Cl.** **C11d 7/50,** C23g 5/02

[58] **Field of Search** 252/171, 364, 66–68; 260/652.5

[56] **References Cited**

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[57] **ABSTRACT**

It is not intended that the following abstract of the disclosure be construed as limiting the invention in any manner.

The disclosure relates to binary azeotropic mixtures of tetrachlorodifluoroethane and methanol. It has also been discovered that n-butanol or isobutanol or sec-butanol will form azeotropes with these halogenated solvents.

The disclosure also relates to ternary azeotropes of tetrachlorodifluoroethane and trichloroethylene with methanol. It has also been discovered that ethanol or isopropanol will also form ternary azeotropes with these two halogenated solvents.

In a further embodiment ternary azeotropes are disclosed comprising tetrachlorodifluoroethane, trichloroethane and methanol. It has also been discovered that ethanol and isopropanol will also form ternary azeotropes with these two halogenated solvents.

3 Claims, No Drawings

AZEOTROPIC COMPOSITION

This is a division of application, Ser. No. 677,715 filed Oct. 24, 1967 now U.S. Pat. No. 3,554,918.

This invention relates to an azeotropic composition and particularly to the binary and ternary azeotropic mixture of tetrachlorodifluoroethane and methanol or any one of the isomers, n-butanol or iso-butanol or sec.-butanol. The present invention also relates to ternary azeotropes of tetrachlorodifluoroethane and trichloroethylene with either methanol or ethanol or isopropanol. In a further embodiment ternary azeotropes have been discovered comprising tetrachlorodifluoroethane, trichloroethane and either methanol or ethanol or isopropanol.

Several of the chlorofluoroethanes have attained widespread use as specialty solvents in recent years, particularly tetrachlorodifluoroethane. This is a relatively high melting compound (CCl_2FCCl_2F, 24.5° C.), which is nontoxic and nonflammable, and which has satisfactory solvent power for greases, oils, waxes and the like under certain conditions. It has therefore found use in cleaning electric motors, compressors, lithographic plates, typewriters, instruments, gauges, and as non-corrosive brines.

For certain solvent purposes however, the chlorofluoroethanes alone have insufficient solvent power. This is particularly true in the electronic industry during the manufacture of "printed circuits." "Printed circuits" are well known in the electronics art; and consist of a circuit formed from a soft metal on a solid, non-conducting surface such as a reinforced phenolic resin. During manufacture, the solid surface is coated with the metal, the desired portion of metal is coated with an impervious coating, and the excess metal is removed by etching with a suitable acid. After the excess metal has been removed, it is necessary to remove the impervious coating because solder joints must be made to the "-printed circuit" and these will not form if the coating is present. After the impervious coating is removed, the circuits are coated with a rosin flux to permit the joints to be soldered, after which the rosin flux must then be removed.

The chlorofluoroethane solvent does not have sufficient solvent power to clean "printed circuits;" that is, to effectively remove the rosin flux. Although mixtures of solvents may be 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. When employing either of these cleaning or degreasing methods the solvent must also be both relatively nontoxic and nonflammable for safety reasons.

Tetrachlorodifluoroethane is a relatively high boiling fluorocarbon and for this reason is especially advantageous in vapor degreasing applications since at these temperatures the hot vapor has more of a tendency to dissolve high melting greases, or fluxes as well as oil residues and the like. 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 up 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 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 have better cleaning power per unit of time in a continuous vapor degreaser than the lower boiling solvents.

Tetrachlorodifluoroethane also is a better solvent than materials such as trichlorotrifluoromethane, 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 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 means of a continuous vapor degreasing machine.

The above object of this invention may be accomplished by a novel binary azeotropic composition of tetrachlorodifluoroethane (e.g. 1,1,2,2-tetrachloro-1,2-difluoroethane) and either methanol or n-butanol or secondary butanol or iso-butanol; ternary azeotropes of tetrachlorodifluoroethane (e.g., 1,1,2,2-tetrachloro-1,2-difluoroethane) trichloroethylene and either methanol or ethanol or isopropanol; and ternary azeotropes of tetrachlorodifluoroethane (e.g. 1,1,2,2-tetrachloro-1,2-difluoroethane), trichloroethane (e.g. 1,1,1-trichloroethane) and either methanol or ethanol or isopropanol. Although 1,1,2,2-tetrachloro-1,2-difluoroethane is a preferred tetrachlorodifluoroethane, the isomer 1,1,1,2-tetrachloro-2,2-difluoroethane may be substituted therefore in whole or in part and especially in minor amounts or trace amounts. The preferred trichloroethane comprises the 1,1,1-trichloroethane isomer. All of these mixtures form azeotropes which distill at a constant temperature, the liquid phase and the vapor phase in equilibrium therewith having the same composition. Such mixture is relatively nonflammable and 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 cleaning electric motors, compressors, lithographic plates, typewriters, precision instruments, gauges, and the like and are particularly useful for cleaning printed circuits.

Although the 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 all 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 three-component or two-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 easily determined once it is known that the halogenated hydrocarbons 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.

EXAMPLE I

An azeotropic composition is obtained in the course of distillation of a mixture of 1,1,2,2-tetrachloro-1,2-difluoroethane and methanol. The mixture is charged to a laboratory distillation flask provided with an overhead condenser for the removal of distillate. The mixture is heated to its atmospheric boiling point and distilled at high reflux. An azeotropic mixture is removed consisting essentially of the following composition:

Components	Composition Percent by Weight	Boiling Point, °F, 760 mm Hg
1,1,2,2-tetrachloro-1,-difluoroethane	69.3	940
methanol	30.7	

EXAMPLES II–X

The method of Example I is repeated using different mixtures of alcohols and/or 1,1,1-trichloroethane or trichloroethylene and 1,1,2,2-tetrachloro-1,2-difluoroethane, the results of which are as follows:

COMPONENTS, PERCENT BY WEIGHT

Example number	1,1,2,2-tetrachloro-1,2-difluoroethane	Methanol	Ethanol	i-Propanol	n-Butanol	i-Butanol	s-Butanol	Trichloroethylene	1,1,1-trichloroethane	Boiling point, ° F.	mm. Hg. pressure
2	93.9				6.1					195	760
3	65					35				191.3	764
4	85						15			189.0	760
5	34.3	30.1						35.6		151	761
6	36.1		25.8					38.2		159.6	764
7	24.3			30.9				44.8		167.7	765
8	4.5	25.9							69.6	131.8	754
9	3.9		18.5						77.6	148.5	763
10	13.8			22.7					63.5	164.3	760

Printed circuit boards are usually prepared by impregnating glass cloth, nylon, or paper laminates with a phenolformaldehyde resin or an epoxy resin. Printed circuits are prepared by a variety of methods. In a typical procedure, the board consists originally of a phenolic resin impregnated base to which is bonded a sheet of copper, 2 to 4-mils thick, covering one surface of the board. The desired circuit is drawn on the copper with an asphalt based ink using the silk screen method. The excess copper is then removed by etching with a ferric chloride-hydrochloric acid bath, sometimes containing ammonium chloride, leaving on the board the copper that is covered by the ink. After washing off the etch solution, the asphalt ink is removed by cleaning with the azeotropic composition of this invention in an ultrasonic bath (some mechanical scrubbing is often used). The entire surface of the board is coated with a rosin flux and dried. The electronic components (resistors, capacitors, etc.) are then added at the proper places for soldering to the circuit. The board is then passed over a molten solder bath, contacting the desired joints with the molten metal, whereby the soldering is effected. After cooling, the excess rosin flux remaining on the board must be removed since, if present in the final assembly, it will lead to corrosion, poor electrical resistance and other deleterious properties.

The board is cleaned by placing it in an ultrasonic bath of any of the aforementioned azeotropes and operating at about 32 kilocycles per second at about 10°–20° F. below the boiling point of the particular azeotrope for about one minute.

When the board is cleaned with the azeotropic mixtures of this invention substantially all of the rosin flux is removed without any detrimental effect on the board which constitutes the backing of the printed circuit.

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.

What is claimed is:

1. An azeotropic composition consisting essentially of about 69 parts, by weight, of 1,1,2,2-tetrachloro-1,2-difluoroethane and about 31 parts methanol.

2. A method for cleaning a solid surface comprising contacting said surface with the composition of claim 1.

3. A method in accordance with claim 2 wherein said composition is in vapor form.

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