

SPECIFICATION Solvent Mixture for Cleaning

The present invention relates to a mixture of solvents for cleaning, and more particularly to a mixture of 1,1,2-trichloro-1,2,2-trifluoroethane (hereinafter referred to as "flon-113"), ethanol, nitromethane and at least one member selected from acetone and acetonitrile in a specific proportion which is analogous to an azeotropic mixture and is particularly suitable for use in electronic industry as a cleaning solvent for removing flux employed in soldering of circuit board.

Hitherto, a binary azeotropic mixture of the flon-113 and ethanol has been employed industrially as a solvent for removing flux. This binary azeotropic mixture is inferior to some extent in its stability when water and a metal are present, and accordingly there has been preferably employed a ternary azeotropic mixture of the flon-113, ethanol and nitromethane in a ratio of 95.3:3.6:1.1 by weight, the boiling point of which is 44.3°C. However, this ternary azeotropic mixture does not always exhibit a satisfactory effect in cleaning power depending on the kind of flux and soldering conditions, e.g. heating temperature.

Accordingly, it is an object of the present invention to provide a cleaning solvent which is particularly suited for use in removing flux.

A further object of the invention is to provide a cleaning solvent having an excellent cleaning power and having no influence upon materials usually used in electronic parts.

Another object of the invention is to provide a cleaning solvent which is easy to recover and is reusable.

These and other objects of the present invention will become apparent from the following description with reference to the accompanying drawings.

It has been found that when 0.3 to 2% by weight of an organic solvent having an excellent dissolving power such as acetone, acetonitrile, ethyl acetate or methylene chloride is added to a mixture of flon-113, ethanol and nitromethane, there can be obtained solvent mixtures which have a good effect on cleaning and removal of flux and exert no bad influence upon materials usually employed in electronic parts, e.g. metals and plastic materials such as polystyrene, polycarbonate and acrylonitrile-butadiene-styrene polymer. However, these mixtures do not form azeotropic mixtures. In general, a solvent mixture which does not show an azeotropic composition not only brings on a change in effective composition during cleaning, but also is very disadvantageous for recovery by distillation and reuse of used mixture. Therefore, in case that a mixture of solvents does not form an azeotropic mixture, it is hard to say that the mixture is a desirable cleaning solvent, even if the mixture has an excellent cleaning effect.

The present inventors have further found that when flon-113, ethanol, nitromethane and at least one member selected from acetone and acetonitrile are admixed in a specified proportion, the obtained mixture has a very advantageous characteristic analogous to an azeotropic mixture and can be available employed as a cleaning solvent.

In accordance with the present invention, there is provided a mixture of solvents for cleaning consisting essentially of 94.1 to 96.3% by weight of 1,1,2-trichloro-1,2,2-trifluoroethane, 3.2 to 4.0% by weight of ethanol, 0.2 to 0.7% by weight of nitromethane and 0.3 to 1.2% by weight of at least one member selected from the group consisting of acetone and acetonitrile. The mixture of the present invention shows an approximately constant boiling point upon rectification, and the distillate has an approximately constant composition throughout the rectification from start to finish.

Figure 1 is a graph showing a relationship between distillation rate, composition of distillate and boiling point of a solvent mixture of the present invention; and

Figures 2 to 5 are graphs showing a relationship between distillation rate, composition of distillate and boiling point of solvent mixtures for comparison.

The present invention is explained below in detail with reference to the accompanying drawings, i.e. graphs showing a relationship of the distillation rate, i.e. percentage of cumulative distillate amount (g.) to charging amount (g.), with the composition of distillate (or vapour) and the boiling point at the time corresponding to the distillation rate, in rectification of a mixture of the present invention and comparative mixtures using a rectifier of 30 plates in number of theoretical plates. In the Figures, the proportion of flon-113 in the distillate is not shown.

A mixture of the present invention shown in Figure 1 consists of 95.5% by weight of flon-113, 3.5% by weight of ethanol, 0.5% by weight of nitromethane and 0.5% by weight of acetone, and the four components of the mixture are distilled at an approximately constant boiling point ranging from 44.1° to 44.7°C in an approximately constant proportion from the initial stage to the end of the distillation. Mixtures containing 0.5% of acetonitrile or a combination of acetone and acetonitrile instead of 0.5% of acetone in the above mixture also show a similar result to that shown in Figure 1, and the boiling point of these mixtures falls within the range of 43.9° to 44.7°C. From these results, it could be understood that the solvent mixture of the present invention has a characteristic which closely resembles an azeotropic mixture.

For the purpose of obtaining a solvent mixture analogous to an azeotropic mixture, it is necessary to admix the four components in a specific proportion, that is to say, to admix flon-113, ethanol,

nitromethane and at least one member selected from acetone and acetonitrile in a ratio of 94.1 to 96.3 : 3.2 to 4.0 : 0.2 to 0.7 : 0.3 to 1.2 by weight, preferably 94.6 to 95.8 : 3.5 to 3.8 : 0.3 to 0.6 : 0.4 to 1.0 by weight. When the proportion of the four or five components does not fall within the above range, no mixture having a similar characteristic to that of an azeotropic mixture is obtained.

Figures 2 and 3 shows the results of rectification of comparative mixtures in which four components used in the present invention are included, but the proportion of acetone or nitromethane is outside the above-mentioned range. The mixture of Figure 2 consists of flon-113, ethanol, nitromethane and acetone in a ratio of 94.0 : 3.5 : 0.5 : 2.0 by weight, and the mixture of Figure 3 consists of flon-113, ethanol, nitromethane and acetone in a ratio of 94.0 : 3.5 : 2.0 : 0.5 by weight.

The composition of the distillate changes with the lapse of time, and it could be understood that these mixtures have not a similar characteristic to an azeotropic mixture.

Figure 4 and 5 also show the results of rectification of comparative mixtures. The mixture of Figure 4 consists of flon-113, ethanol, nitromethane and methylene chloride in a ratio of 95.5 : 3.5 : 0.5 : 0.5 by weight, and the mixture of Figure 5 consists of flon-113, ethanol, nitromethane and ethyl acetate in a ratio of 95.5 : 3.5 : 0.5 : 0.5 by weight. In case of the solvent mixture shown in Figure 4, methylene chloride is easy to distil at the initial stage of the rectification, and nitromethane begins to distil after approximately whole amount of methylene chloride is distilled. In case of the solvent mixture shown in Figure 5, distillation of ethyl acetate is not observed at all in spite of having a lower boiling point than nitromethane. Accordingly, it could be understood that these mixtures also have not a similar characteristic to an azeotropic mixture.

In contrast, the solvent mixture of the present invention shows a distillation characteristic in rectification which is closely similar to an azeotropic mixture of four-components or five-components system. Although the reason is not apparent, the composition of the vapor phase approaches to the composition of the liquid phase only when particularly the content of nitromethane and the ratio of nitromethane to acetone and/or acetonitrile falls within the range in the present invention, so the four or five components form a mixture analogous to an azeotropic mixture. Accordingly, the admixing ratio of the components is important in practising the present invention. In particular, when the content of nitromethane and the content of acetone and/or acetonitrile are outside the range of the present invention, a desirable solvent mixture is not obtained.

The mixture of the present invention is particularly suited for use in removing contaminants, especially flux used in soldering or circuit board. The composition of the mixture may be changed within the before-mentioned range of the composition according to hardness of removing contaminants.

Also, the mixture of the present invention exerts no influence upon materials such as a base material to which a flux is applied. In particular, the use of acetonitrile has the advantages of not only increase of the dissolving power, but also further improving the stabilizing effect on the solvents, especially flon-113 in the presence of metals, especially aluminum, zinc or their alloys.

Since the mixture of the present invention has a similar characteristic to an azeotropic mixture, it is possible to handle it like a single solvent and, therefore, the control of the mixture at the time of use, recovery and reuse are easy, and moreover the mixture does not cause the change in the composition of the components at the time of cleaning or recovery by distillation. Also, the mixture of the invention is usable in any manners of cleaning such as ultrasonic cleaning, dip cleaning, vapor cleaning and spray cleaning, since the mixture does not cause a change in composition by ultrasonic, heating and other thermal and mechanical actions.

The mixture of the present invention is more particularly described and explained by means of the following Examples, in which all % are by weight.

Example 1

A mixture of 95.50% of flon-113, 3.50% of ethanol, 0.50% of nitromethane and 0.50% of acetonitrile was prepared, and a cleaning apparatus was charged with 65.5 kg. of the prepared solvent mixture and was continuously operated for 15 hours to observe that the mixture of the present invention was hard to bring on a change in composition during cleaning.

As a cleaning apparatus, there was employed a double-vessel cleaning apparatus of usual type (Model UP-1210 made by Branson Co., opening portion of dip cleaning vessel: 260x303 mm., opening portion of vapor cleaning vessel: 252x303 mm.) in which a vapor of solvent vaporized in a vapor cleaning vessel was condensed in a cooling zone and introduced into a dip cleaning vessel and the solvent in the dip cleaning vessel is returned to the vapor cleaning vessel by overflowing. In the dip cleaning vessel, cleaning was conducted by means of ultrasonic cleaning.

The cleaning apparatus was operated by heating the vapor cleaning vessel, and a loss percentage of the mixed solvent and the composition of the mixed solvent were measured at intervals of 5 hours.

The loss percentage of the mixed solvent was obtained by measuring the height of the surface of the liquid in the vapor cleaning vessel and calculating according to the following equation:

$$\text{Loss percentage} = \frac{\text{Amount of solvent lost (g.)}}{\text{Amount of solvent charged (g.)}} \times 100$$

The measurement of the composition of the mixed solvent was conducted by gas chromatography with respect to both solvents in the dip and vapor cleaning vessels.
The results are shown in Table 1.

Comparative Example 1

The procedure of Example 1 was repeated except that a mixed solvent of 95.50% of flon-113, 3.50% of ethanol, 0.50% of nitromethane and 0.50% of ethyl acetate was employed.

The results are shown in Table 2.

From Table 2, it would be observed that the mixed solvent brings on a change in composition of the solvent in the dip and vapor cleaning vessels and ethyl acetate is concentrated in the vapor cleaning vessel with the lapse of time.

Table 1

		0	After 5 hrs.	After 10 hrs.	After 15 hrs.
Composition of mixed solvent (%)					
Dip cleaning vessel ...	Flon-113	95.50	95.50	95.52	95.49
	Ethanol	3.50	3.48	3.47	3.47
	Nitromethane	0.50	0.50	0.49	0.51
	Acetonitrile	0.50	0.52	0.52	0.53
Vapor cleaning vessel ...	Flon-113	95.50	95.51	95.49	95.50
	Ethanol	3.50	3.52	3.54	3.54
	Nitromethane	0.50	0.48	0.50	0.49
	Acetonitrile	0.50	0.49	0.47	0.47
Loss percentage		0	4	8	13

Table 2

		0	After 5 hrs	After 10 hrs.	After 15 hrs.
Composition of mixed solvent (%)					
Dip cleaning solvent ...	Flon-113	95.50	95.61	95.73	95.83
	Ethanol	3.50	3.49	3.48	3.47
	Nitromethane	0.50	0.50	0.52	0.52
	Ethyl acetate	0.50	0.40	0.27	0.18
Vapor cleaning solvent ...	Flon-113	95.50	95.33	95.11	94.97
	Ethanol	3.50	3.51	3.53	3.53
	Nitromethane	0.50	0.51	0.53	0.52
	Ethyl acetate	0.50	0.65	0.83	0.98
Loss Percentage		0	4	7	12

Examples 2 to 4

A pre-flux (commercially available under the commercial name "P-52", product of Kabushiki Kaisha Asahi Kagaku Kenkyusho, or the commercial name "A-101B", product of Kabushiki Kaisha Tamura Seisakusho) was applied to the whole surface of a printed-circuit board (60x50 mm) made of a phenol resin on which printed-components were formed. A post-flux (commercially available under the commercial name "JS-64P", product of Kabushiki Kaisha Koki) was further applied to the board, and the board was then placed in an electric furnace at about 250°C for 2 minutes for backing the fluxes.

After taking out from the electric furnace and cooling to room temperature, the printed-circuit board was placed in a cleaning apparatus as used in Example 1 charged with a mixed solvent shown in Table 3. Dip cleaning (ultrasonic cleaning) was conducted for one minute and vapor cleaning was conducted for 30 seconds, and the degree of removal of flux was observed by the naked eye.

The results are shown in Table 3.

Comparative Example 2

The procedure of Examples 2 to 4 was repeated except that a known azeotropic mixture having a composition shown in Table 3 was employed as a cleaning solvent.

The result is shown in Table 3.

Table 3

	Ex. 2	Ex. 3	Ex. 4	Com. Ex. 2
Composition of solvent (%)				
Flon-113 ...	95.3	95.3	95.3	95.3
Ethanol ...	3.6	3.6	3.6	3.6
Nitromethane ...	0.3	0.3	0.3	1.1
Acetone ...	0.8	—	0.4	—
Acetonitrile ...	—	0.8	0.4	—
Degree of removal of flux				
Pre-flux P—52 and post-flux JS—64P ...	complete removal	complete removal	complete removal	locally, thinly remaining (no gloss)
Pre-flux A—101B and post-flux JS—64P ...	complete removal	complete removal	complete removal	thinly remaining nearly all over the surface (no gloss)

Claims

- 20 1. A mixture of solvents for cleaning consisting essentially of 94.1 to 96.3% by weight of 1,1,2-
trichloro-1,2,2-trifluoroethane, 3.2 to 4.0% by weight of ethanol, 0.2 to 0.7% by weight of
nitromethane and 0.3 to 1.2% by weight of at least one member selected from acetone and
acetonitrile. 20
- 25 2. A mixture of solvents for cleaning as claimed in claim 1 substantially as described in any one of
the Examples herein. 25

19



Table 3

	Ex. 2	Ex. 3	Ex. 4	Com. Ex. 2
Composition of solvent (%)				
Flon-113 ...	95.3	95.3	95.3	95.3
Ethanol ...	3.6	3.6	3.6	3.6
Nitromethane ...	0.3	0.3	0.3	1.1
Acetone ...	0.8	—	0.4	—
Acetonitrile ...	—	0.8	0.4	—
Degree of removal of flux				
Pre-flux P—52 and post-flux JS—64P ...	complete removal	complete removal	complete removal	locally, thinly remaining (no gloss)
Pre-flux A—101B and post-flux JS—64P ...	complete removal	complete removal	complete removal	thinly remaining nearly all over the surface (no gloss)

Claims

- 20 1. A mixture of solvents for cleaning consisting essentially of 94.1 to 96.3% by weight of 1,1,2- 20
trichloro-1,2,2-trifluoroethane, 3.2 to 4.0% by weight of ethanol, 0.2 to 0.7% by weight of
nitromethane and 0.3 to 1.2% by weight of at least one member selected from acetone and
acetonitrile.
- 25 2. A mixture of solvents for cleaning as claimed in claim 1 substantially as described in any one of 25
the Examples herein.