

Description

The present invention relates to improved cleaning compositions on the basis of fluorochlorohydrocarbons, alkanols and esters from the group ethyl propionate, methyl propionate and ethyl acetate.

It is generally known also to use mixtures of fluorochlorohydrocarbons (as the main solvent) with a co-solvent in addition to pure chlorinated and/or fluorinated hydrocarbons for industrial cleaning processes or for vapour de-greasing. Such mixtures may be both non-azeotropic and azeotropic or azeotrope-like. "Azeotrope-like" is understood to mean that mixtures boil substantially constantly (change in boiling temperature of not more than 5°C) over a fairly large concentration range and therefore behave similarly to azeotropes for practical use.

A number of efforts have already been made to obtain cleaning compositions with the desired properties. For instance, it is known from DE-OS 29 42 799 to use mixtures of trichlorotrifluoroethane with ethanol and methyl acetate for removing resin soldering fluxes.

However, the known mixtures are still in need of improvement as far as their use properties are concerned. In particular, in conjunction with the further industrial developments in the field of fluxes, new requirements in terms of the removal of these newly developed fluxes have resulted. These requirements are not always fulfilled or often have only been fulfilled unsatisfactorily by the known solvent mixtures. A need for new solvent mixtures with special new properties therefore exists.

It was therefore an object to provide new solvent mixtures which overcome the drawbacks of the prior art and are especially well suited in particular for removing modern fluxes.

5 This object is achieved by the compositions according to the invention, and by the uses and process according to the invention.

10 The subject of the invention is compositions which are distinguished by a content of 98.9 to 45% by weight of a fluorochlorohydrocarbon with 1 to 3 C atoms, 1.0 to 50% by weight of an alkanol with 1 to 4 C atoms and 0.1 to 5% by weight of an ester from the group ethyl propionate, methyl propionate or ethyl acetate. The fluorochlorohydrocarbon constituent in the compositions according to the invention may in this case also be a mixture of different fluorochlorohydrocarbons with 1 to 15 3 C atoms. Likewise, the ester constituent in the compositions according to the invention may also be a mixture of the above-mentioned esters.

20 In a sub-variant of the invention, the compositions are characterised in that they contain 97.5 to 89.0% by weight of the fluorochlorohydrocarbon, 2.0 to 8.0% by weight of the alkanol and 0.5 to 3.0% by weight of the ester.

25 Preferably those fluorochlorohydrocarbons are used which boil within a temperature range of + 20°C to + 120°C at normal pressure. These are known per se and can be taken for instance from Kaltron^R-Taschenbuch, Kali-Chemie AG, 6th edition 1978, pages 14 to 16.

30 Fluorochlorohydrocarbons with 1 to 2 C atoms which are selected from the group trichlorofluoromethane, tetrachlorodifluoroethanes, trichlorotrifluoroethanes, tetrachloromonofluoroethanes, trichlorodifluoroethanes,

dichlorotrifluoroethanes, dichlorodifluoroethanes and dichloromonofluoroethanes are particularly expedient. Compositions with trichlorofluoromethane, tetrachlorodifluoroethanes, trichlorotrifluoroethanes, dichlorotrifluoroethanes and dichloromonofluoroethanes are preferred.

Tetrachlorodifluoroethanes in the spirit of the invention are the isomeric fluoro-chlorohydrocarbons of the empirical formula CCl_4F_2 [sic]. They are thus the fluoro-chlorohydrocarbon 1,1,2,2-tetrachloro-1,2-difluoroethane (R112) and the isomeric 1,1,1,2-tetrachloro-2,2-difluoroethane (R112a) or mixtures thereof.

Trichlorotrifluoroethanes in the spirit of the invention are the isomeric fluoro-chlorohydrocarbons of the empirical formula $\text{C}_2\text{Cl}_3\text{F}_3$. They are thus the fluoro-chlorohydrocarbon 1,1,2-trichloro-1,2,2-trifluoroethane (R113) and the isomeric 1,1,1-trichloro-2,2,2-trifluoroethane (R113a) or mixtures thereof.

Tetrachloromonofluoroethanes in the spirit of the invention are the fluoro-chlorohydrocarbons bearing one hydrogen atom and having the empirical formula $\text{C}_2\text{HCl}_4\text{F}$. They are thus the two not fully-halogenated isomeric fluoro-chlorohydrocarbons 1,1,2,2-tetrachloro-2-fluoroethane (R121) and 1,1,1,2-tetrachloro-2-fluoroethane (R121a) or mixtures thereof.

Trichlorodifluoroethanes in the spirit of the invention are the fluoro-chlorohydrocarbons bearing one hydrogen atom and having the empirical formula $\text{C}_2\text{HCl}_3\text{F}_2$. They are thus the three not fully-halogenated isomeric fluoro-chlorohydrocarbons 1,1,2-trichloro-2,2-difluoroethane (R122), 1,1,2-trichloro-1,2-difluoroethane

(R122a) and 1,1,1-trichloro-2,2-difluoroethane (R122b) or mixtures thereof.

5 Dichlorotrifluoroethanes in the spirit of the invention are the fluorochlorohydrocarbons bearing one hydrogen atom and having the empirical formula $C_2HCl_2F_3$. They are thus the three not fully-halogenated isomeric fluorochlorohydrocarbons 1,1-dichloro-2,2,2-trifluoroethane (R123), 1,2-dichloro-1,1,2-trifluoroethane (R123a) and 1,1-dichloro-1,2,2-trifluoroethane (R123b) or mixtures thereof.

15 Dichlorodifluoroethanes in the spirit of the invention are the fluorochlorohydrocarbons bearing one [sic] hydrogen atom and having the empirical formula $C_2H_2Cl_2F_2$. They are thus the four not fully-halogenated isomeric fluorochlorohydrocarbons 1,2-dichloro-1,2-difluoroethane (R132), 1,1-dichloro-2,2-difluoroethane (R132a), 1,2-dichloro-1,1-difluoroethane (R132b) and 1,1-dichloro-1,2-difluoroethane (R132c) or mixtures thereof.

20 Dichloromonofluoroethanes in the spirit of the invention are the fluorochlorohydrocarbons bearing one [sic] hydrogen atom and having the empirical formula $C_2H_3Cl_2F$. They are thus the three not fully-halogenated isomeric fluorochlorohydrocarbons 1,2-dichloro-1-fluoroethane (R141), 1,1-dichloro-2-fluoroethane (R141a) and 1,1-dichloro-1-fluoroethane (R141b) or mixtures thereof.

30 Particularly preferred compositions contain trichlorofluoromethane (R11), 1,1,2,2-tetrachloro-1,2-difluoroethane (R112), 1,1,2-trichloro-1,2,2-trifluoroethane (R113), 1,1,2,2-tetrachloro-2-fluoroethane (R121), 1,1,2-trichloro-2,2-difluoroethane (R122), 1,1-dichloro-2,2,2-trifluoroethane (R123),

1,2-dichloro-1,2-difluoroethane (R132) and 1,1-dichloro-1-fluoroethane (R141b) as fluorochloro-hydrocarbon. 1,1,2-Trichloro-1,2,2-trifluoroethane (R113), for instance, has proved particularly favourable as the fluorochlorohydrocarbon. However, compositions with 1,1-dichloro-1-fluoroethane (R141b), 1,1-dichloro-2,2,2-trifluoroethane (R123), 1,1,2,2-tetrachloro-1,2-difluoroethane (R112) or trichlorofluoromethane (R11) also yield very good results.

The alkanols with 1 to 4 C atoms used in the compositions according to the invention are selected from the group methanol, ethanol, i-propanol, n-propanol, n-butanol, sec. butanol and tert. butanol, preferably methanol, ethanol and i-propanol. Ethanol has proved particularly favourable. However, methanol or isopropanol are also well suited.

In one very advantageous form of the compositions according to the invention, the latter are characterised by an azeotrope-like behaviour and a content of approximately 94.2% by weight 1,1,2-trichloro-1,2,2-trifluoroethane, 3.5% by weight ethanol and 2.3% by weight ethyl acetate.

The compositions according to the invention are solutions which are clear at room temperature and to which known additives may be added.

One group of known additives are stabilisers. This group comprises those compounds which prevent an unwanted reaction of constituents of the composition with each other or with other reaction participants, such as atmospheric oxygen, water, metal etc. Known stabilisers are for instance nitroalkanes, in particular nitromethane and nitroethane, alkylene

oxides, in particular butylene oxide, or branched alkynols such as 2-methyl-butyn-(3)-ol-(2). These stabilisers may be used alone or in combination, quantities of 0.01 to 5% by weight, preferably 0.05 to 1% by weight, relative to the entire mixture, being very suitable.

Another group of additives comprises known compounds from the group of corrosion inhibitors, non-ionic or ionic emulsifiers and dyeing agents.

The above-named compositions have numerous possible applications in the sector of cleaning and/or vapour de-greasing. In these known processes, the object which is to be cleaned is dipped in liquid and/or vaporious cleaning mixture in one or more stages or is sprayed with liquid cleaning mixture. The cleaning action can be increased in known processes by using elevated temperature and/or ultrasound and/or stirring. Likewise, it is known to improve the cleaning action by mechanical action, for instance brushing.

For example, the electronics industry uses predominantly organic resin fluxes for soldering processes, the surpluses of which have to be removed from printed circuit boards after the soldering operation. This is done using organic solvents which are compatible with the circuit boards and the electronic components, i.e. the solvent must not react therewith. The resin fluxes to be removed are mixtures of polar and non-polar compounds, and often additionally contain special activators. Fluorinated hydrocarbons alone, which are not polar, are not effective at removing the polar constituents of the resins. Known mixtures which contain an alcohol in addition to fluorinated hydrocarbons are just as incapable of fully removing especially high activator-

containing fluxes. However, the compositions according to the invention can remove both the polar and the non-polar constituents and are therefore effective on a wide basis as removers for resin fluxes, in particular for those having a high activator content.

Compositions of R113/ethanol/ethyl acetate, in particular in an azeotrope-like composition of 94.2%/3.5%/2.3%, are particularly well suited for this application. However, other compositions of R113, for instance also with the alcohols methanol or isopropanol and an ester from the group ethyl propionate, methyl propionate or ethyl acetate, give very good results, as do compositions according to the invention with R141b, R123, R112 or R11.

For instance, circuit boards with or without components (and in particular with SMD components) can be cleaned without problems using the compositions according to the invention, even when fluxes having high activator contents are used, without the "white coatings" which are to be feared when using conventional cleaning agents.

The new compositions according to the invention are also desired systems for cooling agents and lubricants, since the compositions have a low surface tension, a low viscosity and for the most part a high density of about 1.4 to 1.6 g/cm³ at 20°C. The above physical properties are those which are desired for lubricant purposes. For instance, the compositions according to the invention are desired if the mixture is used as a lubricant in metal-working machines, such as during drilling, milling, turning, thread-cutting, stamping or the like, where a residue-free surface is necessary. For these applications, known lubricant additives (such as those described in DE-OS 33 42 852 or DE-OS 33 35 870) in particular may also be added.

The low surface tension, and the high wettability and density of the compositions according to the invention make them particularly suitable for cleaning capillary systems.

5 The compositions according to the invention may, for instance, also be used as follows:

- for cleaning hardware or bulk material (preferably in closed units),
- for stripping paint,
- 10 - as special solvents, extraction agents and/or recrystallisation agents in the chemical and pharmaceutical industry.

As was mentioned at the beginning, cleaning compositions which contain 1,1,2-trichloro-1,2,2-trifluoroethane as the fluorochlorohydrocarbon, ethanol as the alkanol and methyl acetate as the ester and which are used for removing resin soldering fluxes are admittedly already known from DE-OS 29 42 799.

15 However, using these methyl acetate-containing compositions does not guarantee in every case the very high degree of cleanness which is required in special fields of use, for instance for cleaning components and printed circuit boards in the electronics industry.

20 Their properties are therefore in part just as inadequate as the fluorochlorohydrocarbon/alkanol compositions without an additive such as methyl acetate known in the prior art. It is therefore all the more surprising that the new mixtures according to the invention, which contain fluorochlorohydrocarbons, 25 alkanols and as an additive the esters ethyl propionate, methyl propionate or ethyl acetate, have superior cleaning properties and are very well suited for the above-mentioned applications. The mixtures according to the invention permit new solutions to 30

problems over a wide field of application. In particular, for instance, also mixtures of 1,1,2-trichloro-1,2,2-trifluoroethane (R113), ethanol and ethyl acetate (see Table 1, No. 15, boiling point approx. 44.3°C) or of 1,1,2-trichloro-1,2,2-trifluoroethane (R113), ethanol and ethyl acetate/-methyl propionate (see Table 1, No. 14, boiling point approx. 45.6°C) have no flash points (open-crucible method).

The following examples are intended to explain the invention in greater detail, but without limiting its scope. Unless stated otherwise, % are always percentages by weight.

Example 1: Cleaning of printed circuit boards

Cleaning tests with printed circuit boards which were contaminated with highly activator-containing solvent fluxes were carried out in a commercially available 2-chamber or 3-chamber cleaning unit. The cleaning compositions, cleaning conditions and cleaning results are given in Table 1.

No.	Compositions for Bath 1	Cleaning conditions	Result
5	1 R141b/ethanol/ methyl propionate: 95.0%/3.0%/2.0%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	+
15	2 R141b/ethanol/ ethyl acetate: 95.0%/3.0%/2.0%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	+
20	3 R141b/methanol/ ethyl acetate: 94.0%/3.7%/2.3%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	++
30	4 R123/ethanol/ ethyl acetate: 95.8%/2.5%/1.7%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	+

5	5	R123/ethanol/ ethyl acetate: 94.2%/3.5%/2.3%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	++
10	6	R123/methanol/ ethyl acetate: 94.2%/3.5%/2.3%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	++
15	7	R113/isopropanol /ethyl acetate: 95.7%/2.3%/2.0%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	+
20	8	R113/isopropanol /ethyl acetate: 47.0%/50.0%/3.0%	3-bath: 1) 3 min. ultra- sound 2) 1 min. ultra- sound 3) 1 min. vapour de-greasing (in bath 2 and 3: R113)	++
25	9	R113/isopropanol: 97.4%/2.6% (azeotropic)	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	-
30				
35				

10	R113/isopropanol: 65.0%/35.0%	3-bath: 1) 3 min. ultra- sound 2) 1 min. ultra- sound 3) 1 min. vapour de-greasing (in bath 2 and 3: R113)	-
5			
10			
11	R113/ethanol/ ethyl propionate: 94.2%/3.5%/2.3%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	++
15			
12	R113/ethanol/ methyl propionate: 93.9%/3.5%/2.6%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	++
20			
25			
13	R113/methyl propionate: 97.3%/2.7% (azeotrope-like)	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	-
30			

5	14	R113/ethanol/ methyl propionate /ethyl acetate: 93.8%/3.4%/1.3%/ 1.5% (azeotrope-like)	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	+
	15	R113/ethanol/ ethyl acetate: 94.2%/3.5%/2.3% (azeotrope-like)	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	++
	16	R113/ethanol: 96.2%/3.8% (azeotropic)	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	-
	17	R113/ethanol/ methyl acetate: 94.2%/3.7%/2.1% (azeotrope-like)	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	-
	18	R113/ethanol/ methyl acetate/ nitromethane: 94.15%/3.7%/2.1%/ 0.05% (azeotrope-like)	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	-

19	R113/ethanol/ ethyl acetate: 68.0%/30.0%/2.0%	3-bath: 1) 3 min. ultra- sound 2) 1 min. ultra- sound 3) 1 min. vapour de-greasing (in bath 2 and 3: R113)	++
5			
10			
20	R113/ethanol: 65.0%/35.0%	3-bath: 1) 3 min. ultra- sound 2) 1 min. ultra- sound 3) 1 min. vapour de-greasing (in bath 2 and 3: R113)	-
15			
20			
21	R113/methanol/ ethyl acetate: 92.5%/6.0%/1.5%	2-bath: 1) 3 min. ultra- sound 2) 1 min. ultra- sound (in bath 2: R113)	++
25			
22	R113/methanol/ ethyl acetate/ nitromethane: 92.2%/6.0%/1.5%/ 0.3%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	++
30			

5	23	R113/methanol: 93.5%/6.5% (azeotropic)	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	-
10	24	R112/ethanol/ ethyl acetate: 94.2%/3.5%/2.3%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	++
15	25	R11/ethanol/ ethyl acetate: 96.5%/2.0%/1.5%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	+
20				
25	26	R11/ethanol/ ethyl acetate: 94.2%/3.5%/2.3%	2-bath: 1) 3 min. ultra- sound 2) 1 min. vapour de-greasing (in bath 2: R113)	++

30 In the cases marked "++" in the "Result" column, a very good cleaning effect was achieved, and a good cleaning effect was achieved in those cases marked "+", and there was no formation of "white coatings". In the cases marked "-", there was formation of "white coatings".

It is clearly apparent that the compositions according to the invention (tests 1 to 8, 11, 12, 14, 15, 19, 21, 22, 24 to 26) are superior to the mixtures according to the prior art (tests 9, 10, 13, 16 to 18, 20 and 23).

5 Example 2: Cleaning of bulk material

1 Bulk material (transistor caps) was cleaned in a 2-chamber unit (3 minutes ultrasound, 1 minute vapour de-greasing) with an azeotrope-like mixture of 94.2% R113, 3.5% ethanol and 2.3% ethyl acetate in order to remove drawing oils. The bulk material was satisfactorily clean after treatment.



Claims

1. Compositions, characterised by a content of 98.9 to 45% by weight of at least one fluorochlorohydrocarbon with 1 to 3 C atoms, 1.0 to 50% by weight of an alkanol with 1 to 4 C atoms and 0.1 to 5% by weight of an ester from the group ethyl propionate, methyl propionate or ethyl acetate, or a mixture of the afore-mentioned esters.

2. Compositions according to Claim 1, characterised in that they contain 97.5 to 89.0% by weight of the fluorochlorohydrocarbon, 2.0 to 8.0% by weight of the alkanol and 0.5 to 3% by weight of the ester.

3. Compositions according to Claim 1 or 2, characterised in that the fluorochlorohydrocarbon in itself has a boiling point in the range of 20°C to 120°C.

4. Compositions according to one of the preceding Claims, characterised in that a fluorochlorohydrocarbon with 1 to 2 C atoms is selected from the group trichlorofluoromethane, tetrachlorodifluoroethanes, trichlorotrifluoroethanes, tetrachloromonofluoroethanes, trichlorodifluoroethanes, dichlorotrifluoroethanes, dichlorodifluoroethanes and dichloromonofluoroethanes, preferably from the group trichlorofluoromethane, tetrachlorodifluoroethanes, trichlorotrifluoroethanes, dichlorotrifluoroethanes and dichloromonofluoroethanes.

5. Compositions according to one of the preceding Claims, characterised in that the fluorochlorohydrocarbon with 1 or 2 C atoms is selected from the group trichlorofluoromethane (R11),



1,1,2,2-tetrachloro-1,2-difluoroethane (R112),
1,1,2-trichloro-1,2,2-trifluoroethane (R113),
1,1,2,2-tetrachloro-2-fluoroethane (R121),
1,1,2-trichloro-2,2-difluoroethane (R122),
5 1,1-dichloro-2,2,2-trifluoroethane (R123),
1,2-dichloro-1,2-difluoroethane (R132) and
1,1-dichloro-1-fluoroethane (R141b).

6. Compositions according to one of the preceding
Claims, characterised in that the alkanol is selected
from the group methanol, ethanol, i-propanol,
n-propanol, n-butanol, sec. butanol and tert. butanol,
preferably methanol, ethanol and i-propanol.

7. Compositions according to one of the preceding
Claims, characterised by an azeotrope-like composition
15 of approximately 94.2% by weight 1,1,2-trichloro-1,2,2-
trifluoroethane (R113), 3.5% by weight ethanol and 2.3%
by weight ethyl acetate.

8. Compositions according to one of the preceding
Claims, characterised by an additional content of
stabiliser of 0.01 to 5% by weight, preferably 0.05 to
1% by weight, relative to the entire mixture,
preferably from the group nitroalkane, alkylene oxide
and/or alkynol.

9. Use of the compositions according to one of the
preceding Claims in immersion and/or spray cleaning
25 processes or for vapour de-greasing.

10. Process for cleaning surfaces, characterised in
that the surfaces, preferably surfaces to be cleaned of
printed circuit boards contaminated with soldering flux
30 or residues of soldering flux, are treated with
compositions according to one of Claims 1 to 8.