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(54) **Solvent cleaning of articles.**

(57) A solvent cleaning composition comprising a mixture preferably an azeotropic, or essentially azeotropic, mixture of dichlorofluoropropane and a chlorinated hydrogen having a boiling point in the range 30°C to 70°C and its use to clean articles.

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This invention relates to solvent cleaning applications in which contaminated articles such as, for example, metals, textiles, glass, plastics, electronic components and printed circuit boards are cleaned using a solvent and/or solvent vapour and more particularly to solvent mixtures useful in solvent cleaning applications and their use.

Solvent cleaning applications wherein contaminated articles are immersed in or washed with halogenated hydrocarbon solvents and/or the vapours thereof are well known and are in common use. Applications involving several stages of immersion, rinsing and drying are common and it is well known to use the solvent at ambient temperature (often accompanied by ultrasonic agitation) or at an elevated temperature up to the boiling point of the solvent. Examples of solvents used in these cleaning processes are 1,1,2-trichloro-1,2,2-trifluoroethane, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene and methylene chloride. These solvents are used alone or in mixtures with cosolvents such as aliphatic alcohols or other low molecular weight, polar additives and depending to some extent upon the articles to be cleaned are often stabilised against degradation induced by light, heat and the presence of metals.

In the known solvent cleaning applications and especially in those applications where the solvent is used at an elevated temperature, there is a tendency for solvent vapour to be lost from the cleaning system into the atmosphere. Further losses may occur in loading and unloading the solvents into cleaning plant and in recovering used solvent by distillation. Whilst care is usually exercised to minimize losses of solvent into the atmosphere, for instance by improved plant design and vapour recovery systems, the expense of totally preventing losses is exorbitant and most practical cleaning applications result in some loss of solvent vapour into the atmosphere.

Until recently, the use of the common cleaning solvents has been regarded as an acceptable practice in that the solvents are stable, non-flammable materials of relatively low toxicity believed to be environmentally benign. However recent evidence suggests that some at least of the common solvents may have a long-term deleterious effect on the stratosphere, the so-called ozone layer, so that replacement solvents are seen to be desirable.

According to the invention there is provided a solvent cleaning composition comprising a mixture of at least one isomer of dichloropentafluoropropane and at least one liquid chlorinated hydrocarbon having a boiling point in the range of 30°C to 70°C.

The dichloropentafluoropropane may be a mixture of isomers but preferably contains at least a major proportion of 1,1-dichloro-2,2,3,3,3-pentafluoropropane, which is known in the art as "225ca", 1,3-dichloro-1,2,2,3,3-pentafluoropropane, which is known in the art as "225cb", is another useful isomer.

The chlorinated hydrocarbon preferably boils at a temperature in the range of 40°C to 65°C and preferably contains at least one hydrogen atom in the molecule. Examples of suitable chlorinated hydrocarbons include saturated and ethylenically unsaturated aliphatic compounds which may be cyclic or acyclic. Whilst any chlorinated hydrocarbon of appropriate boiling point may be employed, we prefer compounds containing less than six carbon atoms, especially compounds containing two, three or four carbon atoms. The compound should contain at least one chlorine atom and preferably contains at least two chlorine atoms. Specific examples of suitable chlorinated hydrocarbons are dichloroethane and dichloroethylene, particularly 1,1-dichloroethane and trans-1,2-dichloroethylene. The cleaning composition may contain more than one chlorinated hydrocarbon.

Suitable chlorinated hydrocarbons for use in the solvent compositions include the following:-

	B. Pt. (°C)
2-chloropropane	36
methylene chloride	40
5 1-chloropropane	47
<u>trans</u> -1,2-dichloroethylene	47
2-chloro-2-methyl propane	51
10 (t-butyl chloride)	
1,1-dichloroethane	57
<u>cis</u> -1,2-dichloroethylene	60
chloroform	62
15 1-chloro-2-methyl propane	69
(1-chloroisobutane)	
2,2-dichloropropane	70

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We have found that dichloropentafluoropropane and especially 1,1-dichloro-2,2,3,3,3-pentafluoropropane, forms azeotropic mixtures with at least some chlorinated hydrocarbons and whilst the ability to form an azeotropic mixture is not an essential feature of the invention, chlorinated hydrocarbons which form an azeotropic mixture are preferred. By way of example, 1,1-dichloro-2,2,3,3,3-pentafluoropropane forms binary azeotropes with 1,1-dichloroethane and with trans-1,2-dichloroethylene.

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1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,1-dichloroethane form a binary azeotrope, or essentially azeotropic mixture, consisting of about 80.5% by weight of the halogenated propane and about 19.5% by weight of 1,1-dichloroethane and having a boiling point of about 51.4°C.

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1,1-dichloro-2,2,3,3,3-pentafluoropropane forms a binary azeotrope, or essentially azeotropic mixture, with trans-1,2-dichloroethylene consisting of about 52% by weight of the halogenated propane, and about 48% by weight of the dichloroethylene and having a boiling point of about 45.4°C. The azeotrope is a preferred cleaning composition according to the present invention.

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Whilst an azeotropic mixture may be preferred since it maintains an essentially constant composition in use, we have found that some non-azeotropic mixtures, for example containing about 18% by weight of 1,1-dichloro-2,2,3,3,3-pentafluoro-propane, do in fact exhibit acceptable compositional stability in use and may be attractive in affording the possibility of controlling the cleaning power of the solvent cleaning composition.

The amounts of dichloropentafluoropropane and chlorinated hydrocarbon in the mixture may vary within wide limits but the mixture should contain sufficient dichloropentafluoropropane to render the mixture non-flammable so that it does not have a flash point.

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The mixture preferably contains at least 15% by weight of dichloropentafluoropropane. Useful mixtures comprise from 15% to 90% by weight of dichloropentafluoropropane. It is often preferred that the mixture contains from 20% to 80% by weight. However, we have found that at less than 20% w/w the dichloropentafluoropropane is an effective diluent for dichloroethane.

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We have found two preferred mixtures for replacing the commonly used solvents 1,1,2-trichloro-1,2,2-trifluoroethane and 1,1,1-trichloroethane. One such mixture comprises about 50:50% by weight of the dichloropentafluoropropane and 1,1-dichloroethane; the second such mixture comprises about 18:82% by weight of dichlorofluoropropane:1,1-dichloroethane.

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In addition to dichloropentafluoropropane and the chlorinated hydrocarbon, the cleaning composition may contain an aliphatic hydrocarbon and/or a polar compound, for example an aliphatic alcohol, preferably an alcohol containing from 2 to 6 carbon atoms. Methanol, ethanol and propanol (n-propanol or iso-propanol), are preferred, especially ethanol. The amount of the alcohol may be up to 50% by weight of the composition, although amounts below about 10% are preferred. A typical ternary or quaternary mixture contains from about 2% to about 7% by weight of alcohol.

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1,1-dichloro-2,2,3,3,3-pentafluoropropane, at least some chlorinated hydrocarbons and some at least of the lower alkanols form azeotropes and such ternary azeotropes represent another preferred feature of the invention, particularly in boiling-solvent cleaning applications.

The azeotrope of 1,1-dichloro-2,2,3,3,3-pentafluoropropane, 1,1-dichloroethane and methanol boils at 46.4°C and consists of 76.3% by weight the halogenated propane, 17.7% by weight of 1,1-dichloroethane and

6% by weight of methanol. The ternary azeotrope containing ethanol boils at 51°C and consists of 79% by weight of the dichloropentafluoropropane, 18% by weight of 1,1-dichloroethane and 3% by weight of ethanol.

The azeotrope of 1,1-dichloro-2,2,3,3,3-pentafluoropropane, trans-1,2-dichloroethylene and methanol boils at 41.2°C and consists of 41.1% by weight of the halopropane, 52.7% by weight of the dichloroethylene and 62% by weight of methanol. The ternary azeotrope containing ethanol boils at 44.4°C and consists of 47.7% by weight of the halopropane, 49.4% by weight of the dichloroethylene and 2.9% by weight of ethanol.

1,1-dichloroethane and trans-1,2-dichloroethylene form a ternary azeotrope with 1,1-dichloro-2,2,3,3,3-pentafluoropropane. This ternary azeotrope boils at 52.6-52.7°C and contains 47.9% by weight of trans-1,2-dichloroethylene but only 0.2% by weight of 1,1-dichloroethane.

As stated, the cleaning composition may contain an aliphatic hydrocarbon, acyclic or cyclic saturated or ethylenically unsaturated hydrocarbons being examples of suitable components. Suitable hydrocarbons, which should be liquids at room temperature, include those having a boiling point in the range 30°C to 75°C, preferably 40°C to 65°C. A particularly suitable hydrocarbon for use with 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,1-dichloroethane or trans-1,2-dichloroethylene is cyclopentane, b.p 50°C, although the compounds may not form ternary azeotropes.

As examples of suitable hydrocarbons for incorporation in the solvent cleaning compositions according to the present invention may be mentioned inter alia:

	B.Pt (°C)
2-methylbutane (isopentane)	30
2-methyl but-1-ene (amylene)	31
pentane	35-36
2-methyl but-2-ene	35-38
cyclopentane	50
2,2-dimethylbutane (neohexane)	50
4-methyl pent-1-ene	53-54
3-methyl pent-1-ene	54
<u>cis</u> -4-methyl pent-2-ene	57-58
2,3-dimethyl butane	58
2-methyl pentane (isohexane)	61
2-methyl pent-1-ene	62
3-methyl pentane	63
2-methyl-pent-2-ene	67
n-hexane	69
3-methyl pent-2-ene	69
methyl cyclopentane	72

The amount of the hydrocarbon in the solvent cleaning composition may vary within wide limits, for example from 20% to 80% by weight. However, hydrocarbons are generally readily flammable and the amount of the hydrocarbon should preferably be such that the composition remains non-flammable. In particular, the combined amount of hydrocarbon and chlorinated hydrocarbon (and alcohol if present) should preferably be below that at which the composition is flammable and exhibits a flash point. In addition to the requirement that the liquid composition be non-flammable, any vapours emitted during use of the composition should preferably also be non-flammable.

The compositions of the invention may contain one or more stabilisers as are often used in previous cleaning compositions, notably nitroalkanes and epoxides.

The cleaning compositions of the invention may be used as replacements for the solvents used in any of the known cleaning applications and a process is provided according the invention for cleaning articles which

comprises contacting the article(s) with the cleaning composition and/or the vapour thereof. The compositions may be used in cold cleaning applications but will usually be employed at an elevated temperature up to their boiling points.

The invention is illustrated but in no way limited by the following Examples.

EXAMPLES 1-2

These Examples illustrate the use of azeotropic mixtures according to the present invention for the removal of flux from printed circuit boards.

The azeotropic mixtures described in Table 1 were used to remove ionic solder flux residues from circuit boards by the following procedure.

A known weight of solder cream was applied to test boards (5 cm x 7 cm) cut from a copper-coated FR4 board and reflowed in a Micro VPS unit. The solder cream was a 62% tin/38% lead solder available as Multicore PRAB 3.

The solvent was boiled in a beaker fitted with an upper cooling coil through which cold water was circulated to create a boiling liquid phase and a vapour phase. The contaminated test board was dipped into the boiling liquid for 60 seconds and then held in the vapour for 30 seconds.

Residual ionic contamination of the test board, expressed as mg sodium chloride per square centimetre, was determined using a Protonique Contaminometer. The ionic contamination of an unwashed test board was determined and the % removal of ionic contamination by the cleaning procedure was calculated.

The results are shown in Table 1.

Table 1

Example No	Solvent			Ionic contaminants removed (%)
	225ca (%)	1,1-dichloroethane (%)	1,2-trans-dichloroethylene (%)	
1	80.5	19.5	0	72.4
2	52	0	48	77.3

EXAMPLES 3-5

These Examples illustrate the use of ternary azeotropic mixtures according to the present invention for the removal of flux from printed circuit boards.

The test procedure described in Examples 1-2 was repeated using the ternary azeotropes described in Table 2. The results obtained are shown in Table 2.

TABLE 2

EXAMPLE NO.	TERNARY SOLVENT					Ionic Contaminant Removed %
	Dichloro- pentafluoro- propane		1,1-dichloro- ethane %	1,2-trans- dichloro- ethylene %	Ethanol %	
	225ca %	225cb %				
3	79	0	18	0	3	68.7
4	47.7	0	0	49.4	2.9	80.4
5	0	66.4	29.2	0	4.4	84.9

EXAMPLE 6

This example illustrates the compatibility of solvent cleaning compositions according to the present invention with plastics materials.

5 Samples of three plastics materials (A-C) were thoroughly dried by heating in an oven at 80°C for 1 hour followed by standing in a dessicator for a minimum of 24 hours.

The samples were removed from the dessicator, weighed immediately and then immersed in the boiling solvent for 30 minutes (± 5 seconds) after which time they were removed and allowed to cool in air for 5 minutes and then weighed. The samples were then placed in a dessicator for 24 hours before being re-weighed. The results are shown in Table 3.

The plastics materials tested were:-

A - Polypropylene copolymer [LYM 123]

B - Nylon [Maranyl A125]

15 C - epoxy/glass fibre laminate [FR4]

The solvents used in the tests were:-

I - An 80:20% by weight mixture of 1,1-dichloro-2,2,3,3,3-pentafluoropropane (DCPFP) and 1,1-dichloroethane (DCE).

II - A 60:40% by weight mixture of DCPFP and DCE.

III - A 20:80% by weight mixture of DCPFP and DCE.

20 IV - A 79:18:3% by weight mixture of DCPFP, DCE and ethanol.

V - A 48:49:3% by weight mixture of DCPFP, 1,1-dichloro-ethane and ethanol.

A comparative test was carried out using as solvent:-

VI - 1,1,2-trichloro-1,2,2-trifluoroethane.

TABLE 3

PLASTIC	A		B		C	
SOLVENT	% Weight Change after 30 mins immersion					
	5 min	24 hr	3 min	24 hr	5 min	24 hr
I	+1.10	+0.55	-0.01	-0.02	-0.01	0
II	+1.98	+0.88	0	+0.01	+0.02	+0.02
III	+3.54	+1.35	0	-0.01	+0.62	+0.37
IV	+0.97	+0.49	+0.03	0	+0.03	0
V	+4.05	+1.50	+0.07	+0.04	+0.85	+0.42
VI Comparison	+1.31	+0.57	-0.02	-0.02	0	-0.01

EXAMPLES 7-8

These Examples illustrate the stability of solvent cleaning compositions according to the present invention against degradation in the presence of aluminium, zinc and mild steel.

5 Nitromethane (0.3% by weight) was added to the azeotropic mixtures of dichloro-pentafluoropropane (80.5%) and 1,1-dichloroethane (19.5%) described in Table 4 and the solvent (50 ml) was charged to a reflux apparatus heated on an oil bath.

10 Weighed test pieces of aluminium, zinc and mild steel were located in the reflux apparatus, partly immersed in the boiling solvent. After approximately 3 days the metal test pieces and the solvent were removed for analysis. The metal pieces were washed with a small amount of deionised water (which was retained and used later to extract ionic species from the used solvent), rinsed with more water and brushed free of any deposits. They were then rinsed with acetone, dried and re-weighed.

The used solvent was extracted with the metal rinse water (see above) and the extract was analysed for chloride and fluoride ions.

15 The results were that no change in weight was detected in any of the metal test pieces and no change in halide ion content was detected in the solvent. There was no change in the GC trace for the solvent.

The mild steel test pieces were clean and bright and there was no visual evidence of a tidemark corresponding to the liquid/vapour interface. The aluminium test pieces and the zinc test pieces were also clean and bright although a very slight tidemark was observed on each test piece.

TABLE 4

EXAMPLE NO.	AZEOTROPIC MIXTURE			
	DICHLORO- PENTAFLUORO- PROPANE		1,1-DICHLORO- ETHANE	ETHANOL
	225ca (%)	225cb (%)		
7	80.5	0	19.5	0
8	0	66.4	29.2	4.4

Claims

1. A solvent cleaning composition comprising a mixture of at least one isomer of dichloropentafluoropropane and at least one liquid chlorinated hydrocarbon having a boiling point in the range of 30°C to 70°C.
2. A solvent cleaning composition as claimed in Claim 1 wherein a major proportion of the dichloropentafluoropropane is 1,1-dichloro-2,2,3,3,3-pentafluoropropane.
3. A solvent cleaning composition as claimed in Claim 1 wherein the chlorinated hydrocarbon boils at a temperature in the range of 40°C to 65°C.

4. A solvent cleaning composition as claimed in Claim 3 wherein the chlorinated hydrocarbon contains less than 6 carbon atoms.
- 5 5. A solvent cleaning composition as claimed in Claim 3 wherein the chlorinated hydrocarbon contains at least two chlorine atoms.
6. A solvent cleaning composition as claimed in Claim 1 wherein the chlorinated hydrocarbon has at least one hydrogen atom in the molecule.
- 10 7. A solvent cleaning composition as claimed in Claim 1 wherein the mixture comprises 15% to 90% w/w dichloropentafluoropropane.
8. A solvent cleaning composition as claimed in Claim 2 wherein the chlorinated hydrocarbon forms an azeotropic, or essentially azeotropic, mixture with 1,1-dichloro-2,2,3,3,3- pentafluoropropane.
- 15 9. A solvent cleaning composition as claimed in Claim 1 further comprising a liquid aliphatic hydrocarbon or a polar compound or both.
10. A solvent cleaning composition as claimed in claim 9 wherein the polar compound is an aliphatic alcohol containing from 2 to 6 carbon atoms.
- 20 11. A solvent cleaning composition as claimed in Claim 10 wherein the mixture forms a ternary azeotropic, or essentially azeotropic, mixture.
- 25 12. A solvent cleaning composition as claimed in Claim 9 comprising 1,1-dichloro-2,2,3,3,3-pentafluoropropane, trans-1,2-dichloroethylene and pentane,
13. A solvent cleaning composition as claimed in Claim 2 wherein the at least one chlorinated hydrocarbon comprises a mixture of trans-1,2-dichloroethylene and 1,2-dichloroethane.
- 30 14. A process for cleaning articles which comprises contacting the article(s) with the solvent composition as claimed in Claim 1, or the vapour thereof, or both.
15. A process for cleaning articles as claimed in Claim 14 carried out at elevated temperature.

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