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(54) Solvent cleaning of articles.

(57) A solvent cleaning composition comprising a mixture, preferably an azeotropic or substantially azeotropic mixture, of dichloropentafluoropropane and 1,1-dichloroethane 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.

5 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,
10 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
15 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
20 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
25 desirable.

According to the invention there is provided a solvent cleaning composition comprising a mixture of at least one isomer of dichloropentafluoropropane and 1,1-dichloroethane.

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".

30 1,3-dichloro-1,2,2,3,3-pentafluoropropane which is known in the art as "225cb", is another useful isomer.

1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,1-dichloroethane form an azeotrope or essentially azeotropic mixture and the azeotrope is a preferred cleaning composition according to the invention, particularly in boiling-solvent cleaning applications. The azeotrope consists of about 80.5% by weight 1,1-dichloro-2,2,3,3,3-pentafluoropropane and about 19.5% by weight 1,1-dichloroethane and has a boiling point of about 51.4°C.

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

The amounts of dichloropentafluoropropane and 1,1-dichloroethane in the mixture may vary within wide
40 limits but the mixture should contain sufficient dichloropentafluoropropane to render the mixture non-flammable so that it does not have a flash point.

The mixture should contain at least 15% by weight of the 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 of the dichloropentafluoropropane. However, we have found that at less than 20%
45 w/w the dichloropentafluoropropane is an effective diluent for 1,1-dichloroethane.

There are two preferred mixtures for replacing the presently 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 other comprises about 18:80% by weight dichloropentafluoropropane: 1,1-dichloroethane.

50 In addition to dichloropentafluoropropane and 1,1-dichloroethane, 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 mixture contains from about 2% to about 7% by weight of
55 alcohol.

1,1-dichloro-2,2,3,3,3-pentafluoropropane, 1,1-dichloroethane 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 containing methanol boils at about 46.4°C and consists

of about 76.3% by weight the dichloropentafluoropropane, about 17.7% by weight of 1,1-dichloroethane and about 6% by weight of methanol. The azeotrope containing ethanol boils at about 51°C and consists of about 79% by weight of the dichloropentafluoropropane, about 18% by weight of 1,1-dichloroethane and about 3% by weight of ethanol. On the other hand, a ternary azeotrope containing propanol does not appear to be produced.

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 is cyclopentane, b.p 50°C, although the compounds do not appear to form a ternary azeotrope.

As examples of suitable hydrocarbons for incorporation in the solvent cleaning composition 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 1,1-dichloroethane, which is also flammable, 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 known 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.

EXAMPLE 1

This Example illustrates the use of an azeotropic mixture according to the present invention for the removal of flux from a printed circuit board.

5 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,1-dichloroethane (80.5% halopropane/19.5% haloethane) was 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.

10 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
15 determined and the % removal of ionic contamination by the cleaning procedure was calculated. 72.4% of ionic contaminants were removed.

EXAMPLES 2-3

20 These Examples illustrate the use of ternary azeotropic mixtures according to the present invention for the removal of ionic solder flux from a printed circuit board.

The test procedure described in Example 1 was repeated using the ternary azeotropes described in Table
1.

The results obtained are shown in Table 1.

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TABLE 1

Example No	Ternary Azeotrope			Flux Removal		
	Dichloro- pentafluoro-propane		1, 1-Dichloro-ethane	Ethanol	Ionic Contaminant Removed	Appearance of Product
		225ca (%)	225cb (%)	(%)	(%)	
2	79	0	18	3	68.7	c&b
3	0	66.4	29.2	4.4	84.9	c&b

c&b : Clean and bright

EXAMPLE 4

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

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 2.

The plastics materials tested were:-

A - Polypropylene copolymer [LYM 123]

B - Nylon [Maranyl A125]

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.

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

In a Comparative Test,

V - 1,1,2-trichloro-1,2,2-trifluoroethane, was used as solvent.

TABLE 2

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 Comparative Test	+1.31	+0.57	-0.02	-0.02	0	-0.01

EXAMPLE 5-6

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.

Nitromethane (0.3% by weight) was added to the azeotropic mixtures described in Table 3 and the resulting solvents (50 ml) were charged to a reflux apparatus heated on an oil bath.

Weighed test pieces of aluminium, zinc and mild steel were located in the reflux apparatus, partly immersed
5 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
10 chloride and fluoride ions.

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
15 bright although a very slight tidemark was observed on each test piece.

TABLE 3

Example No	Azeotropic Mixture			
	Dichloropenta- fluoropropane		1,1-Dichloro- ethane	Ethanol
	225ca (%)	225cb (%)		
5	80.5	0	19.5	0
6	0	66.4	29.2	4.4

Claims

1. A solvent cleaning composition comprising a mixture of at least one isomer of dichloropentafluoropropane and 1,1-dichloroethane.
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 2 comprising up to about 20% w/w 1,1-dichloro-ethane.
4. A solvent composition as claimed in Claim 1 containing from 15-90% w/w of dichloropentafluoropropane.
5. A solvent composition as claimed in Claim 2 wherein the 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,1-dichloroethane are in the form of an azeotropic or substantially azeotropic mixture.
6. A solvent composition as claimed in Claim 1 further comprising an aliphatic hydrocarbon or polar organic

compound or both.

7. A solvent composition as claimed in Claim 6 wherein the polar organic compound is an alcohol containing 2 to 6 carbon atoms.

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8. A solvent composition as claimed in Claim 7 containing up to about 10% w/w of the alcohol.

9. A solvent composition as claimed in Claim 7 wherein 1,1-dichloro-2,2,3,3,3-pentafluoroethane, 1,1-dichloroethane and the alcohol form an azeotrope.

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10. A solvent composition as claimed in Claim 9 wherein the alcohol is methanol or ethanol.

11. A solvent composition as claimed in Claim 6 comprising 1,1-dichloro-2,2,3,3,3-pentafluoropropane, 1,1-dichloroethane and cyclopentane.

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12. A process for cleaning articles which comprises contacting the article(s) with the solvent composition claimed in Claim 1, or the vapour thereof, or both.

13. A process for cleaning articles as claimed in Claim 12 carried out at elevated temperature.

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