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D-8000 München 86(DE)(54) **Flux removal solvent blend.**

(57) Superior solder flux (e.g., rosin flux) removal compositions are disclosed which have no flash point. These compositions consist of 0.5 to less than about 2 percent methanol with 3 to 10 percent of one or more alcohols containing 2-5 carbon atoms the balance being an optionally inhibited 1,1,1-trichloroethane.

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FLUX REMOVAL SOLVENT BLEND

The electronics industry requires circuit boards which are substantially free of ionic and organic flux residues since such contribute to failure of the circuit board in use. Therefore, stringent methods are employed to clean the boards of both ionic and organic residues. Numerous solvents and mixtures of solvents have been tried and rejected. The most widely used commercial solvent is 1,1,2-trifluoro-1,2,2-trichloroethane (Fluorocarbon 113) in admixture with 10.67 volume percent methanol and 0.33 volume percent nitromethane. This solvent effectively cleans from the soldered circuit board the rosin flux soldering aids. The cleaning effectiveness is measured by standard procedures in the industry, one of which is set by the U.S. military which is a specification for "Printed Wiring Assemblies" MIL-P-28809. This test consists of spraying or immersing the cleaned board in a freshly prepared aqueous isopropyl alcohol solution for a specified period of time after which the resistivity of the solution is measured in units of ohm-cm. The

effectiveness of a flux removal blend is a function of the cleaning time, flux composition and the type of cleaning operation. All these being equal, the more effective blends will give a higher specific resistance value when tested according to the above test or similar standard test.

The above mentioned fluorochlorocarbon blend has been shown by industrial experience and by means of the above test to be an effective flux removal solvent. Generally, chlorinated hydrocarbons alone or in combination with alkanols below the flash point level give poorer results, particularly with respect to removal of ionic components of the flux. It is important that the blends used by the industry have no flash point for obvious safety reasons.

It is also known that chlorinated hydrocarbons, especially 1,1,1-trichloroethane (methylchloroform), will remove the nonionic components of the rosin flux solder aids better than the aforementioned fluorochlorocarbon blend.

Two patents disclosing flux removing compositions are U.S. 3,932,297 and 4,023,984, claiming 1,1,1-trichloroethane (methylchloroform) with 1-propanol (n-propyl alcohol) and 2-propanol (isopropyl alcohol), respectively; and an azeotropic composition of a fluorocarbon and 1-butanol (n-butyl alcohol) is disclosed in U.S. 3,671,446 as useful in cleaning circuit boards.

It, therefore, would be advantageous to have a chlorinated solvent composition which will effectively remove both ionic and nonionic flux residues and has no

flash point. The present invention provides such a composition.

According to the invention, stable 1,1,1-trichloroethane (methylchloroform) solvent compositions in combination with from 0.5 to less than 2 percent by volume of methanol and from about 3 to about 10 percent by volume of at least one alcohol having from 2 to 5 carbon atoms have proven to be superior flux removal solvents. These compositions also have no flash point.

10 A series of experiments were carried out employing several formulations of chlorinated hydrocarbons and a 1,1,2-trifluoro-1,2,2-trichloroethane formulation which is widely used by industry to remove flux residues from circuit boards.

15 Test Procedure

Coupons of electronic circuit board base material measuring 1" x 1" x 1/16" (25.4 mm x 25.4 mm x 1.6 mm) were cleaned by immersion in two clean baths of 75 volume percent 2-propanol (isopropyl alcohol) and 25 volume percent water, agitated by an ultrasonic vibrator. The clean coupons were placed in a nitrogen dry box until used.

Each clean coupon was removed from the dry box and immediately immersed horizontally into an Alpha 711-35 MIL flux for five minutes. The Alpha 711-35 MIL flux is widely used by circuit board manufacturers, and is well known to those skilled in the art. The coupons were then hung horizontally to dry for five minutes.

Thereafter, the coupon was heated in a horizontal position in an oven at 250°C for 15 seconds to simulate actual use conditions. After heating, the coupon was again hung in a nitrogen dry box until used in the cleaning experiments.

In conducting the cleaning comparisons, a flux coated coupon taken from the dry box was hung from a clip and (1) introduced into a vapor zone of the flux removal solvent formulation for thirty (30) seconds, (2) immersed in the boiling solvent for thirty (30) seconds, (3) raised above the vapor zone into the free board area above the vapor zone for thirty (30) seconds, then (4) back into the vapor zone for a final thirty (30) seconds and (5) removed to a hanger to dry.

Each coupon after drying was tested for cleanliness by immersing the coupon in 40 ml of a pure solvent consisting of an admixture of 2-propanol (isopropyl alcohol) and water, 75/25 volume percent, respectively, while the solvent was subjected to ultrasonic vibration for five (5) minutes. Upon removal of the coupon, the resistivity of the aqueous alcohol solution was measured using a clean 1 mm conductivity bridge for each measurement. The mean result of several measurements for each of the enumerated formulations was obtained. The higher the resistivity value, the more effective is the removal of the ionic flux residues.

A second test was conducted on the flux removal blends with respect to their resistance to corrosion of aluminum. The test consisted of placing aluminum (Al 2024) shavings in a flask containing the

liquid solvent blend. A condenser was attached to the flask and the solvent heated to boiling and refluxed by the condenser for a period of seven days, during which time observations were made of the shavings. If no corrosion of the aluminum was observed by the end of seven days, the blend was considered to have passed the test.

The flash point of each blend was also determined. (The method used was ASTM-92 known as the Cleveland Open Cup flash point method.) If the blend had a flash point, it was considered to have failed. No observable flash point indicates the solvent passed, or was acceptable. The results of flash point and corrosion tests are given in Table I, failed and passed being indicated by F and P, respectively.

Comparative Example 1

The above test procedures were conducted using a commercially available inhibited 1,1,1-trichloroethane (methylchloroform) consisting of:

95.7% 1,1,1-trichloroethane
0.7% 1,2-Butylene oxide
0.4% Nitromethane
3.2% Diethylene ether.

Comparative Example 2

A commercially available flux removal blend was also tested as above. The blend consisted of:
89% Fluorocarbon 113 (described above)
10.67% Methanol
0.33% Nitromethane.

Comparative Example 3

The above test was also performed using the inhibited methylchloroform of Comparative Example 1 (92.5 percent) with 7.5 percent 2-butanol, which is
5 also a commercially available product.

Percentages in Examples 1-3 above as well as succeeding examples are all by volume unless otherwise indicated.

Table I shows the results of testing for the
10 blends of Comparative Examples 1-3 above and others known to the art. Comparative Examples 7-13 employ 10 percent of several different alcohols with the inhibited of Comparative Example 1.

TABLE I

Ex. No.	Blend ¹			FP ²	Al Corro- sion	Specific Resistance ³ (x 10 ⁶ ohm-cm)	
	MeOH (%)	2BOH (%)	MBY (%)				
5	C-1	--	--	--	P	P	0.2
	C-2	10.67	--	--	P	P	1.5
	C-3	--	7.5	--	P	P	0.8
	C-4	1	--	--	P	P	1.1
	C-5	2	--	--	F	P	1.8
10	C-6	--	--	12	F	P	--
	C-7	--	--	10	P	P	0.6
	C-8	--	10	--	F	P	0.9
	C-9	Ethanol 10%			F	F	1.5
	C-10	Isopropanol 10%			F	F	1.3
15	C-11	Isobutanol 10%			--	--	0.9
	C-12	Tert-butanol 10%			--	--	0.6
	C-13	Dowanol PM ⁴ 10%			--	--	0.5

MEOH = methanol, 2BOH = 2-butanol, MBY = 2-methyl-3-butyn-2-ol

¹ Volume percent additives, balance being the blend of Comparative Example 1. Other components of Comparative Examples 1, 2 and 3 are shown preceding Table I.

² Cleveland Open Cup Flash Point

³ Test Method - Modified from "A Comparison of Removal of Activated Rosin Flux by Selected Solvents," Technical Paper by Turbini, Engle, and Stark, Western Electric Company, Princeton, N.J., U.S.A.

⁴ Trademark of The Dow Chemical Company for the mono-methylether of propylene glycol.

It should be noted that Comparative Examples 1-13 are comparative in nature and do not fall within the scope of the invention.

The inhibited methylchloroform of Comparative Example 1 is not effective in removing ionic components of the flux. Comparative Examples 2 and 3 demonstrate the present state of the art in cleaning ionic residues with commercially available blends which do not have a flash point. It is apparent that the fluorochlorocarbon blend is more effective than the butanol-1,1,1-trichloroethane blend. It is also apparent from Examples 4-13 that a single alcohol blended with 1,1,1-trichloroethane will not yield a formulation which will give comparable results to the fluorinated blend and still have no flash point. Comparative Examples 4 and 5 show that 1 percent methanol in 1,1,1-trichloroethane gives no flash point whereas 2 percent methanol has a flash point.

A number of stabilized 1,1,1-trichloroethane (Comparative Example 1) flux-removal compositions containing various amounts of methanol together with other alcohols were tested on the same flux as above in accordance with the above described procedures. Results are shown in Table II as Examples 14-35. These examples show that some 1,1,1-trichloroethane blends with methanol, 2-butanol and/or 2-methyl-3-butyn-2-ol which have no flash point unexpectedly have better ionic residual flux removal performance than the fluorochlorocarbon blend of Comparative Example 2. The preferred blends contain about 1 percent methanol and about 6 percent of 2-butanol and/or 2-methyl-3-butyn-2-ol. The blends containing 0.5 percent methanol are slightly inadequate in their ionic residual flux removal and the blends

approaching 2 percent methanol are too close to the undesirable flash point region.

Those samples exhibiting a flash point are considered to not be within the scope of the invention.

- 5 The blend judged to be most preferred is 1 percent methanol, 3 percent 2-butanol and 3 percent 2-methyl-3-butyn-2-ol.

Importantly, specific resistance values are comparable only with other values derived using substantially identical test conditions. Thus, for example, the data for Table II are not comparable with those from Table III because a different flux was used. For the test conditions employed for the Data in Table II, those compositions having a specific resistance of $\geq 1.1 \times 10^6$ ohm-cm are preferred, while those having a value of ≥ 15 are most preferred.

With respect to solvency for the rosin flux components, when the volume of methanol is comparatively low the volume of the other alcohol component or mixture needs to be higher in order to effect the removal of ionic components. When the methanol volume approaches 2 percent, the other component can be present in minimal quantities. Two percent or more of methanol gives a product which has a flash point and thus is outside the scope of the invention.

These compositions, as do all 1,1,1-trichloroethane compositions which may be employed in contact with metals, especially aluminum, should be stabilized to be commercially practical. Any of a number of compounds are useful as stabilizers, including

diethylene ether (1,4-dioxane), dioxolanes, nitro-
alkanes, 1,2-butylene oxide and the like. These are
well known to the art-skilled and have substantially no
adverse effect on the flux removal properties. Since
5 the known stabilized 1,1,1-trichloroethane compositions
do not completely remove the ionic flux components, it
is necessary to add other solvents to them to provide
for more complete removal of these ionics. The present
invention provides such compositions which are shown in
10 Table II and described in the above Summary of the
Invention.

TABLE II

	Example No.	MeOH (%)	2BOH (%)	MBY (%)	FP	Specific Resistance (x 10 ⁶ ohm-cm)
5	14	0.5	3	--	P	0.2
	15	0.5	5	--	P	0.4
	16	0.5	--	4	P	0.6
	17	0.5	8	--	P	0.6
	18	0.5	10	--	P	1.4
10	19	0.5	--	6	P	1.4
	20	0.5	--	8	P	1.4
	21	1.0	1	--	P	0.9
	22	1.0	3	--	P	1.6
	23	1.0	5	--	P	1.9
15	24	1.0	8	--	P	2.4
	C-25	1.0	--	4	F*	0.9
	26	1.0	--	6	P	1.6
	27	1.0	--	8	P	1.6
	28	1.0	2	2	P	1.3
20	29	1.0	2	3	P	1.6
	30	1.0	3	2	P	1.6
	C-31	1.0	2	4	F*	2.0
	32	1.0	3	3	P	2.1
	33	1.0	4	2	P	1.2
25	34	1.0	4	3	P	1.2
	C-35	1.0	4	4	F*	1.9
	C-36	2.0	6	--	F*	3.2
	C-37	2.0	--	4	F*	1.5
	C-38	2.0	--	6	F*	2.1

30 Those examples whose number is preceded by "C-" are not within the scope of the invention due to their flash point.

Some of the blends tested above and others in which methanol and other alcohols are used were tested on a different flux (Alpha 711) which contained more ionic components than that previously tested. The results are shown in Table III.

TABLE III
Alpha 711 Flux

	Example No.	MeOH (%)	2BOH (%)	MBY (%)	Other# (%)	FP	Specific Resistance (x 10 ⁵ ohm-cm)
10	39	1	3	3	--	P	1.0
	40	--	--	--	--	P	0.2
	41	--	3	3	--	P	0.5
	42	0.5	--	6	EtOH (1)	P	1.4
15	43	0.5	6	--	2-PrOH (2)	P	0.8
	44	1.0	--	3	2M2BOH (3)	P	1.1
20	45	--	--	3	2M2BOH (3)	--	0.3

#EtOH = ethanol; 2-PrOH = 2-propanol; 2M2BOH = t-amyl alcohol

Table III again shows the poor performance of stabilized 1,1,1-trichloroethane alone. The alcohol blends containing no methanol also show low effectiveness as compared to the methanol blends of the present invention. It is noted that since Alpha 711 flux contains 50 percent solids as opposed to 35 percent solids for 711-35 MIL it is more difficult to clean using the same set of conditions, this is reflected in the lower specific resistance values obtained.

1. A 1,1,1-trichloroethane rosin flux removal composition characterized in that it

(A) contains, based on the total volume of the composition,

(i) from 0.5 to less than about 2 volume percent methanol, and

(ii) from 3 to 10 volume percent of at least one alcohol having from 2 to 5 carbon atoms; and

(B) has no flash point as measured by the Cleveland Open Cup method.

2. The composition of Claim 1 wherein component A(ii) is 2-butanol.

3. The composition of Claim 1 wherein component A(ii) is 2-methyl-3-butyn-2-ol.

4. The composition of Claim 1 wherein component A(ii) is a mixture of 2-butanol and 2-methyl-3-butyn-2-ol.

5. The composition of Claim 4 wherein the volumes of said butanol and methylbutynol are equal.

6. The composition of Claim 4 wherein the total volume of component A(ii) is from 6 to 10 volume percent.

7. The composition of Claim 1 wherein component A(ii) is a mixture of ethanol and 2-methyl-3-butyn-2-ol.

8. The composition of Claim 1 wherein component A(ii) is a mixture of 2-butanol and 2-propanol.

9. The composition of Claim 1 wherein component A(ii) is a mixture of 2-methyl-3-butyn-2-ol and 2-methyl-2-butanol.

10. The composition of Claim 4 wherein the methanol is present at from 0.5 to 1 volume percent.

11. The composition of Claim 1 wherein the composition has a specific resistance of at least 1.1×10^6 ohm·cm as determined by the method of Examples 1-38.

12. The composition of Claim 1 wherein the composition has a specific resistance of at least 1.5×10^6 ohm·cm as determined by the method of Examples 1-38.

13. The method of Claim 1 in which additionally contains a component to stabilize the 1,1,1-trichloroethane so as to avoid corrosion of aluminum.



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EUROPEAN SEARCH REPORT

0108422

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 83111161.2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 7)
X	DE - A - 2 214 597 (SOLVAY & CIE.) * Page 2, especially last paragraph; claims *	1-3, 7-9, 13	C 23 G 5/02 C 11 D 7/26 C 11 D 7/30 C 11 D 7/50
Y	EP - A1 - 0 044 111 (SOLVAY & CIE.) * Page 2, line 9 - page 3, line 15; examples; claims *	1-4,6, 9,13	C 11 D 7/60
Y	GB - A - 2 069 995 (CHEMISCHE WERKE KLUTHE GMBH & CO.) * Abstract; page 1, lines 6-9; claims *	1	
D,Y	US - A - 4 023 984 (J.J. CLEMENT-SON et al.) * Column 2, lines 15-47; claims *	1,2, 13	TECHNICAL FIELDS SEARCHED (Int. Cl. 7) C 23 G C 11 D
Y	US - A - 3 974 230 (W.L. ARCHER et al.) * Abstract; column 8, lines 37-60; claims *	1,13	
D,Y	US - A - 3 932 297 (J.J. CLEMENT-SON et al.) * Column 2, lines 26-56; claims *	1,2, 13	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 30-12-1983	Examiner SLAMA
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



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