

This Sheet Has Been Replaced



REPLACED SHEETS	
☒ Description	: paged 1 to paged 36
☒ Claim(s)	: paged 31 to paged 35
☒ Drawing(s)	: paged 4 to paged 7
☒ Abstract	: paged 4 to paged 7
DATE OF RECEIPT	

1

A COMPOSITION AND A PROCESS FOR REMOVING ROSIN SOLDER FLUX WITH
TERPENE AND HYDROCARBONS

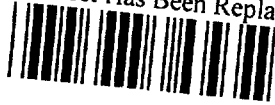
5

FIELD OF THE INVENTION

The present invention relates to processes for removing adherent soils from substrates. More specifically, the invention relates to effective cleaning processes which utilize non-azeotropic mixtures of solvating agents and rinsing agents.

The present invention provides cleaning methods having characteristics and features which are highly desirable in numerous and varied commercial applications. For example, most metallic components are treated with an oil or other processing agent during the fabrication process, and this oil must be removed before the component is installed in the finished product. It is also frequently required that excess rosin flux must be removed from printed circuit boards before the boards are acceptable for use. The present processes are adaptable for use in these and many other applications. Thus, although the present invention is described initially herein in connection with its applicability to the cleaning of printed circuit boards, it will be appreciated from a reading of the entire application that the invention has wider application.

Printed circuit boards typically consist of a rigid or flexible sheet of fiberglass-reinforced dielectric plastic having electrical contacts and conductors on one or both sides thereof. Electrical components are electrically connected to these connectors and/or contacts using any one of a number of soldering techniques. Most of the soldering techniques currently used in commercial manufacturing processes include the step of coating the entire circuit



side of the printed circuit board, or at least a portion thereof, with a solder flux prior to carrying out the actual soldering step. Rosin flux is commonly used alone or in combination with activating amine-based additives, such as amine hydrochloride, to clean the conductive metal parts and to promote strong mechanical and electrical bond with the solder.

After the soldering process is complete, the presence of residual flux on the printed circuit board is detrimental to the operability of the electrical circuitry and components contained on the board. Accordingly, any residual flux present on the board must be removed.

REPORTED DEVELOPMENTS

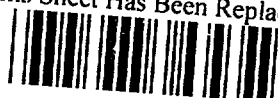
The techniques used to remove adherent residues from printed circuit boards are numerous and varied, ranging from simple brushing of the board with solvent to relatively sophisticated emulsion cleaning. See Leonida, Handbook of Printed Circuit Design, Manufacture, Components and Assembly, Chapter 9, pp. 464-489 (1981). One of the most widely used cleaning techniques is known as vapor degreasing or vapor-liquid-vapor cleaning. According to this process, the printed circuit board is contacted in succession by: (1) relatively hot solvent-containing vapors; (2) by relatively cool solvent-containing liquid; and (3) finally by relatively hot solvent-containing vapor.

Equipment typically used in connection with vapor degreasing consists of a two-section tank. The first section of the tank contains boiling solvent and the second section of the tank contains relatively cool, non-boiling solvent. Refrigerated coils are provided in the vapor space above the boiling solvent, and solvent vapor condenses onto the coils and is transferred to the cold solvent in the second section of the tank. A certain portion of the cold liquid solvent is returned to the first section of the tank to maintain a sufficient quantity of

boiling liquid solvent. The cleaning process typically proceeds by first introducing a relatively cold, soil-containing circuit board into the vapor space above the boiling solvent. Due to the temperature difference between the circuit board and the solvent vapor, solvent condenses on the printed circuit board and achieves a solvating action on the residual rosin fluxes. The condensed vapors and the rosin fluxes solvated thereby are allowed to return to the first section of the tank. After the desired amount of cleaning action has occurred, the board is then moved to the second section of the tank and immersed in the cold solvent, thereby cooling the board and effecting any final cleaning which may be desired. The relatively cool board is then introduced once again into the relatively hot vapor space, where condensing vapors perform a final rinse on the board. Such vapor-liquid-vapor cleaning processes are described on pages 475-477 of Leonida. According to the teachings of Leonida, vapor degreasing processes require solvents having a boiling point of below about 75°C (167°F).

The types of materials that have heretofore been used for the removal of residual fluxes from printed circuit boards are also numerous and varied. For example, chlorinated hydrocarbons, aliphatic hydrocarbons, alcohols, and terpenes are known rosin flux solvents. Because of their high vapor pressures and good solvating ability in the vapor state, chlorinated hydrocarbons, including chlorofluorocarbons, have been widely used in vapor degreasing type processes. However, chlorinated hydrocarbons are generally relatively poor solvents for any ionic residues which may be present on the printed circuit board or other substrate to be cleaned. See Leonida, page 466. For this and other reasons, chlorinated hydrocarbons in general, and chlorofluorocarbons in particular, have sometimes been used in combination with other low-boiling solvents.

This Sheet Has Been Replaced





Mixtures comprising chlorinated hydrocarbons and other low-boiling solvents have been suggested for use in vapor degreasing type processes. In general, however, the prior art has failed to suggest, and in some cases has even discouraged, the use of mixtures having components with widely different vapor pressures in vapor degreasing processes. This has been especially true for prior art directed to the use of solvent mixtures which include chlorinated hydrocarbons, as illustrated, for example, in U.S. Patent No. 3,640,884 - Scholfield et al:

Although mixtures of solvents have been used for [removing rosin flux from printed circuit boards] they have the disadvantage that they boil over a range of temperatures and consequently undergo fractionation in vapor degreasing or ultrasonic applications which are open to the atmosphere.

(Col. 1, lines 47-51). Accordingly, Schofield requires the use of tetrachlordifluoroethane in the form of binary and ternary azeotropic mixtures for use as solvents in vapor degreasing processes. Other patents which disclose the use of azeotropic mixtures containing chlorinated hydrocarbons as solvents in vapor degreasing type cleaning processes are U.S. Patent Nos. 3,960,746 - Gorski; 3,733,218 - Begun; and 4,062,795 - Hutchinson.

While chlorinated hydrocarbons and mixtures containing chlorinated hydrocarbons have been used widely and with advantage as solvents in printed circuit board cleaning processes, the use of such materials has recently been strongly discouraged for environmental reasons. In particular, the use of chlorinated hydrocarbons, including chlorofluorocarbons, has been severely criticized by ecologists because the dispersal of such materials into the atmosphere has been found to damage the ozone layer. For this reason, the use of chlorinated hydrocarbons has been greatly restricted and, in some situations, prohibited entirely. Thus, despite their attractive solvency characteristics, chlorinated hydrocarbons are no longer the



solvent of choice in vapor degreasing processes. Thus, a need now exists for an alternative to the typical prior art degreasing processes, which rely heavily on chlorinated hydrocarbons for effective cleaning.

5

SUMMARY OF THE INVENTION

Applicants have discovered cleaning processes in which adherent soils are effectively removed from substrates. In particular, the present processes generally comprise (a) contacting the substrate with a liquid solvating agent and, preferably simultaneously and/or subsequently, (b) contacting the substrate with a rinsing agent, the ratio of the vapor pressure of said rinsing agent to the vapor pressure of said solvating agent being relatively high, preferably no less than about 20.

According to one preferred aspect of the present invention, the contacting step (a) comprises contacting the substrate with a boiling liquid cleaning composition comprising the solvating agent and the rinsing agent described above. Because of the extreme difference in volatility between the solvating and rinsing agents, the solvating agent has a strong tendency to remain in the liquid phase, and the vapor space overlying the boiling liquid contains only very minor amounts of the solvating agent and relatively high concentrations of the rinsing agent. This is an extremely advantageous condition since the need to recover and recycle the solvating agent is minimized according to the preferred process of the present invention. Moreover, due to the relatively non-volatile nature of the solvating agent, concern about possible escape of harmful solvating materials into the atmosphere is substantially reduced or eliminated.

According to another preferred aspect of the invention, the contacting step (b) comprises contacting the substrate with a vapor comprising the rinsing agent. This step is especially preferred for use in connection with the

5 A particularly preferred embodiment of the present invention comprises a cleaning composition in which the solvating agent and the rinsing agent are immiscible with each other. Advantages associated with the use of such a composition are described below.

FIG. 1 is a semi-schematic view of a preferred apparatus used in connection with the present methods.

The present invention utilizes a combination of process steps and processing agents to effectively remove adherent soils from substrates. The term "substrate" is used herein in a broad sense to designate any device or article of manufacture which may be subject to contamination by unwanted materials. Thus, the term "substrate" encompasses, for example, machine parts, tools, component assemblies and printed circuit boards. Likewise, the term "adherent soil" is also used in a broad sense to designate, for example, unwanted materials which are not easily removed from the substrate by ordinary mechanical means. Thus, the term "adherent soil" encompasses inorganic and organic materials, for example, greases, waxes, oils, adhesives and rosin fluxes. Applicants contemplate, however, that the invention will find particular utility in connection with the cleaning of rosin fluxes from printed circuit boards and in connection with cleaning of wax, grease and/or oils from machine parts.

The present methods comprise the step of contacting the substrate to be cleaned with a liquid solvating agent.

In this context, the term "solvating agent" refers to components or mixtures of components which have a strong tendency to solvate the adherent soil. The solvating agents of the invention preferably have a solvating power at room temperature of at least about 10, and even more preferably of at least about 20. Solvating power is determined by measuring the parts by weight of adherent soil dissolvable in 100 parts by weight of solvating agent at room temperature. According to especially preferred
5
10
15
20
25
30
embodiments, the adherent residue is substantially fully miscible in the solvating agent in substantially all proportions.

An important feature of the present invention is the use of a solvating agent that has a relatively low vapor pressure. Applicants have discovered that the use of low
15
20
25
30
vapor pressure solvating agents in combination with other preferred features of the present invention provides cleaning methods which are at once highly effective and environmentally benign. In particular, the low vapor pressure solvating agents have a strong tendency to remain in the liquid state. A principal disadvantage of prior chlorinated hydrocarbon solvents was the tendency of such compounds to escape into the environment. Furthermore, the strong tendency of the present solvating agents to remain in the liquid state greatly simplifies process design. Accordingly, in one embodiment of the present invention the solvating agents preferably have a room temperature vapor pressure of not greater than about 0.05 atmosphere (about 40 mm Hg), and even more preferably not greater than about 0.01 atmosphere (about 8 mm Hg). The term "room
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
200
205
210
215
220
225
230
235
240
245
250
255
260
265
270
275
280
285
290
295
300
305
310
315
320
325
330
335
340
345
350
355
360
365
370
375
380
385
390
395
400
405
410
415
420
425
430
435
440
445
450
455
460
465
470
475
480
485
490
495
500
505
510
515
520
525
530
535
540
545
550
555
560
565
570
575
580
585
590
595
600
605
610
615
620
625
630
635
640
645
650
655
660
665
670
675
680
685
690
695
700
705
710
715
720
725
730
735
740
745
750
755
760
765
770
775
780
785
790
795
800
805
810
815
820
825
830
835
840
845
850
855
860
865
870
875
880
885
890
895
900
905
910
915
920
925
930
935
940
945
950
955
960
965
970
975
980
985
990
995
1000
1005
1010
1015
1020
1025
1030
1035
1040
1045
1050
1055
1060
1065
1070
1075
1080
1085
1090
1095
1100
1105
1110
1115
1120
1125
1130
1135
1140
1145
1150
1155
1160
1165
1170
1175
1180
1185
1190
1195
1200
1205
1210
1215
1220
1225
1230
1235
1240
1245
1250
1255
1260
1265
1270
1275
1280
1285
1290
1295
1300
1305
1310
1315
1320
1325
1330
1335
1340
1345
1350
1355
1360
1365
1370
1375
1380
1385
1390
1395
1400
1405
1410
1415
1420
1425
1430
1435
1440
1445
1450
1455
1460
1465
1470
1475
1480
1485
1490
1495
1500
1505
1510
1515
1520
1525
1530
1535
1540
1545
1550
1555
1560
1565
1570
1575
1580
1585
1590
1595
1600
1605
1610
1615
1620
1625
1630
1635
1640
1645
1650
1655
1660
1665
1670
1675
1680
1685
1690
1695
1700
1705
1710
1715
1720
1725
1730
1735
1740
1745
1750
1755
1760
1765
1770
1775
1780
1785
1790
1795
1800
1805
1810
1815
1820
1825
1830
1835
1840
1845
1850
1855
1860
1865
1870
1875
1880
1885
1890
1895
1900
1905
1910
1915
1920
1925
1930
1935
1940
1945
1950
1955
1960
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
2020
2025
2030
2035
2040
2045
2050
2055
2060
2065
2070
2075
2080
2085
2090
2095
2100
2105
2110
2115
2120
2125
2130
2135
2140
2145
2150
2155
2160
2165
2170
2175
2180
2185
2190
2195
2200
2205
2210
2215
2220
2225
2230
2235
2240
2245
2250
2255
2260
2265
2270
2275
2280
2285
2290
2295
2300
2305
2310
2315
2320
2325
2330
2335
2340
2345
2350
2355
2360
2365
2370
2375
2380
2385
2390
2395
2400
2405
2410
2415
2420
2425
2430
2435
2440
2445
2450
2455
2460
2465
2470
2475
2480
2485
2490
2495
2500
2505
2510
2515
2520
2525
2530
2535
2540
2545
2550
2555
2560
2565
2570
2575
2580
2585
2590
2595
2600
2605
2610
2615
2620
2625
2630
2635
2640
2645
2650
2655
2660
2665
2670
2675
2680
2685
2690
2695
2700
2705
2710
2715
2720
2725
2730
2735
2740
2745
2750
2755
2760
2765
2770
2775
2780
2785
2790
2795
2800
2805
2810
2815
2820
2825
2830
2835
2840
2845
2850
2855
2860
2865
2870
2875
2880
2885
2890
2895
2900
2905
2910
2915
2920
2925
2930
2935
2940
2945
2950
2955
2960
2965
2970
2975
2980
2985
2990
2995
3000
3005
3010
3015
3020
3025
3030
3035
3040
3045
3050
3055
3060
3065
3070
3075
3080
3085
3090
3095
3100
3105
3110
3115
3120
3125
3130
3135
3140
3145
3150
3155
3160
3165
3170
3175
3180
3185
3190
3195
3200
3205
3210
3215
3220
3225
3230
3235
3240
3245
3250
3255
3260
3265
3270
3275
3280
3285
3290
3295
3300
3305
3310
3315
3320
3325
3330
3335
3340
3345
3350
3355
3360
3365
3370
3375
3380
3385
3390
3395
3400
3405
3410
3415
3420
3425
3430
3435
3440
3445
3450
3455
3460
3465
3470
3475
3480
3485
3490
3495
3500
3505
3510
3515
3520
3525
3530
3535
3540
3545
3550
3555
3560
3565
3570
3575
3580
3585
3590
3595
3600
3605
3610
3615
3620
3625
3630
3635
3640
3645
3650
3655
3660
3665
3670
3675
3680
3685
3690
3695
3700
3705
3710
3715
3720
3725
3730
3735
3740
3745
3750
3755
3760
3765
3770
3775
3780
3785
3790
3795
3800
3805
3810
3815
3820
3825
3830
3835
3840
3845
3850
3855
3860
3865
3870
3875
3880
3885
3890
3895
3900
3905
3910
3915
3920
3925
3930
3935
3940
3945
3950
3955
3960
3965
3970
3975
3980
3985
3990
3995
4000
4005
4010
4015
4020
4025
4030
4035
4040
4045
4050
4055
4060
4065
4070
4075
4080
4085
4090
4095
4100
4105
4110
4115
4120
4125
4130
4135
4140
4145
4150
4155
4160
4165
4170
4175
4180
4185
4190
4195
4200
4205
4210
4215
4220
4225
4230
4235
4240
4245
4250
4255
4260
4265
4270
4275
4280
4285
4290
4295
4300
4305
4310
4315
4320
4325
4330
4335
4340
4345
4350
4355
4360
4365
4370
4375
4380
4385
4390
4395
4400
4405
4410
4415
4420
4425
4430
4435
4440
4445
4450
4455
4460
4465
4470
4475
4480
4485
4490
4495
4500
4505
4510
4515
4520
4525
4530
4535
4540
4545
4550
4555
4560
4565
4570
4575
4580
4585
4590
4595
4600
4605
4610
4615
4620
4625
4630
4635
4640
4645
4650
4655
4660
4665
4670
4675
4680
4685
4690
4695
4700
4705
4710
4715
4720
4725
4730
4735
4740
4745
4750
4755
4760
4765
4770
4775
4780
4785
4790
4795
4800
4805
4810
4815
4820
4825
4830
4835
4840
4845
4850
4855
4860
4865
4870
4875
4880
4885
4890
4895
4900
4905
4910
4915
4920
4925
4930
4935
4940
4945
4950
4955
4960
4965
4970
4975
4980
4985
4990
4995
5000
5005
5010
5015
5020
5025
5030
5035
5040
5045
5050
5055
5060
5065
5070
5075
5080
5085
5090
5095
5100
5105
5110
5115
5120
5125
5130
5135
5140
5145
5150
5155
5160
5165
5170
5175
5180
5185
5190
5195
5200
5205
5210
5215
5220
5225
5230
5235
5240
5245
5250
5255
5260
5265
5270
5275
5280
5285
5290
5295
5300
5305
5310
5315
5320
5325
5330
5335
5340
5345
5350
5355
5360
5365
5370
5375
5380
5385
5390
5395
5400
5405
5410
5415
5420
5425
5430
5435
5440
5445
5450
5455
5460
5465
5470
5475
5480
5485
5490
5495
5500
5505
5510
5515
5520
5525
5530
5535
5540
5545
5550
5555
5560
5565
5570
5575
5580
5585
5590
5595
5600
5605
5610
5615
5620
5625
5630
5635
5640
5645
5650
5655
5660
5665
5670
5675
5680
5685
5690
5695
5700
5705
5710
5715
5720
5725
5730
5735
5740
5745
5750
5755
5760
5765
5770
5775
5780
5785
5790
5795
5800
5805
5810
5815
5820
5825
5830
5835
5840
5845
5850
5855
5860
5865
5870
5875
5880
5885
5890
5895
5900
5905
5910
5915
5920
5925
5930
5935
5940
5945
5950
5955
5960
5965
5970
5975
5980
5985
5990
5995
6000
6005
6010
6015
6020
6025
6030
6035
6040
6045
6050
6055
6060
6065
6070
6075
6080
6085
6090
6095
6100
6105
6110
6115
6120
6125
6130
6135
6140
6145
6150
6155
6160
6165
6170
6175
6180
6185
6190
6195
6200
6205
6210
6215
6220
6225
6230
6235
6240
6245
6250
6255
6260
6265
6270
6275
6280
6285
6290
6295
6300
6305
6310
6315
6320
6325
6330
6335
6340
6345
6350
6355
6360
6365
6370
6375
6380
6385
6390
6395
6400
6405
6410
6415
6420
6425
6430
6435
6440
6445
6450
6455
6460
6465
6470
6475
6480
6485
6490
6495
6500
6505
6510
6515
6520
6525
6530
6535
6540
6545
6550
6555
6560
6565
6570
6575
6580
6585
6590
6595
6600
6605
6610
6615
6620
6625
6630
6635
6640
6645
6650
6655
6660
6665
6670
6675
6680
6685
6690
6695
6700
6705
6710
6715
6720
6725
6730
6735
6740
6745
6750
6755
6760
6765
6770
6775
6780
6785
6790
6795
6800
6805
6810
6815
6820
6825
6830
6835
6840
6845
6850
6855
6860
6865
6870
6875
6880
6885
6890
6895
6900
6905
6910
6915
6920
6925
6930
6935
6940
6945
6950
6955
6960
6965
6970
6975
6980
6985
6990
6995
7000
7005
7010
7015
7020
7025
7030
7035
7040
7045
7050
7055
7060
7065
7070
7075
7080
7085
7090
7095
7100
7105
7110
7115
7120
7125
7130
7135
7140
7145
7150
7155
7160
7165
7170
7175
7180
7185
7190
7195
7200
7205
7210
7215
7220
7225
7230
7235
7240
7245
7250
7255
7260
7265
7270
7275
7280
7285
7290
7295
7300
7305
7310
7315
7320
7325
7330
7335
7340
7345
7350
7355
7360
7365
7370
7375
7380
7385
7390
7395
7400
7405
7410
7415
7420
7425
7430
7435
7440
7445
7450
7455
7460
7465
7470
7475
7480
7485
7490
7495
7500
7505
7510
7515
7520
7525
7530
7535
7540
7545
7550
7555
7560
7565
7570
7575
7580
7585
7590
7595
7600
7605
7610
7615
7620
7625
7630
7635
7640
7645
7650
7655
7660
7665
7670
7675
7680
7685
7690
7695
7700
7705
7710
7715
7720
7725
7730
7735
7740
7745
7750
7755
7760
7765
7770
7775
7780
7785
7790
7795
7800
7805
7810
7815
7820
7825
7830
7835
7840
7845
7850
7855
7860
7865
7870
7875
7880
7885
7890
7895
7900
7905
7910
7915
7920
7925
7930
7935
7940
7945
7950
7955
7960
7965
7970
7975
7980
7985
7990
7995
8000
8005
8010
8015
8020
8025
8030
8035
8040
8045
8050
8055
8060
8065
8070
8075
8080
8085
8090
8095
8100
8105
8110
8115
8120
8125
8130
8135
8140
8145
8150
8155
8160
8165
8170
8175
8180
8185
8190
8195
8200
8205
8210
8215
8220
8225
8230
8235
8240
8245
8250
8255
8260
8265
8270
8275
8280
8285
8290
8295
8300
8305
8310
8315
8320
8325
8330
8335
8340
8345
8350
8355
8360
8365
8370
8375
8380
8385
8390
8395
8400
8405
8410
8415
8420
8425
8430
8435
8440
8445
8450
8455
8460
8465
8470
8475
8480
8485
8490
8495
8500
8505
8510
8515
8520
8525
8530
8535
8540
8545
8550
8555
8560
8565
8570
8575
8580
8585
8590
8595
8600
8605
8610
8615
8620
8625
8630
8635
8640
8645
8650
8655
8660
8665
8670
8675
8680
8685
8690
8695
8700
8705
8710
8715
8720
8725
8730
8735
8740
8745
8750
8755
8760
8765
8770
8775
8780
8785
8790
8795
8800
8805
8810
8815
8820
8825
8830
8835
8840
8845
8850
8855
8860
8865
8870
8875
8880
8885
8890
8895
8900
8905
8910
8915
8920
8925
8930
8935
8940
8945
8950
8955
8960
8965
8970
8975
8980
8985
8990
8995
9000
9005
9010
9015
9020
9025
9030
9035
9040
9045
9050
9055
9060
9065
9070
9075
9080
9085
9090
9095
9100
9105
9110
9115
9120
9125
9130
9135
9140
9145
9150
9155
9160
9165
9170
9175
9180
9185
9190
9195
9200
9205
9210
9215
9220
9225
9230
9235
9240
9245
9250
9255
9260
9265
9270
9275
9280
9285
9290
9295
9300
9305
9310
9315
9320
9325
9330
9335
9340
9345
9350
9355
9360
9365
9370
9375
9380
9385
9390
9395
9400
9405
9410
9415
9420
9425
9430
9435
9440
9445
9450
9455
9460
9465
9470
9475
9480
9485
9490
9495
9500
9505
9510
9515
9520
9525
9530
9535
9540
9545
9550
9555
9560
9565
9570
9575
9580
9585
9590
9595
9600
9605
9610
9615
9620
9625
9630
9635
9640
9645
9650
9655
9660
9665
9670
9675
9680
9685
9690
9695
9700
9705
9710
9715
9720
9725
9730
9735
9740
9745
9750
9755
9760
9765
9770
9775
9780
9785
9790
9795
9800
9805
9810
9815
9820
9825
9830
9835
9840
9845
9850
9855
9860
9865
9870
9875
9880
9885
9890
9895
9900
9905
9910
9915
9920
9925
9930
9935
9940
9945
9950
9955
9960
9965
9970
9975
9980
9985
9990
9995
10000
10005
10010
10015
10020
10025
10030
10035
10040
10045
10050
10055
100

of the substrate or the components thereof. With respect to substrates comprising a printed circuit board, the solvating agent is preferably inert with respect to and not a solvent for epoxy resin impregnated fiberglass. The present solvating agents also preferably are low in viscosity to improve processing characteristics and low in toxicity to improve safety characteristics. It is highly preferred that the solvating agents of the present invention are benign to the atmosphere, soil and water. Chemical and photochemical stability are also other preferred features of the present solvating agents.

The solvating agent of the present invention is preferably selected from the group consisting of terpenes, dibasic esters, monobasic esters, petroleum solvents, alkyl substituted 2-pyrrolidones, ketones, ethers, alcohols, amines and mixtures of two or more of the aforementioned, with terpenes being preferred for adherent soils comprising rosin flux. While it is contemplated that all terpene and terpene-based compounds are adaptable for use as solvating agents according to the present invention, it is especially preferred that the solvating agent be selected from the group consisting of alpha pinene, beta pinene, gamma terpinene, delta-3-carene, limonene, dipentene, terpinolene and a mixture of two or more of the aforementioned, with limonene and dipentene being preferred. As will be seen from examples reported below, particularly good results have been achieved also with the use of organic esters.

The present methods also require contacting the substrate with a rinsing agent. As the term is used herein, rinsing agent refers to a component or mixture of components characterized by an ability to wash solvating agent, and any adherent residue dissolved thereby, from the substrate. Other characteristics of the rinsing agent will vary widely, depending upon factors such as substrate type and the solvating agent being used, and all such rinsing agents are within the scope of the present invention.



According to a preferred embodiment hereof, the rinsing agent has a vapor pressure at room temperature which is high relative to the vapor pressure at room temperature of the solvating agent. More particularly, it is preferred that the ratio of the vapor pressure of the rinsing agent to the vapor pressure of the solvating agent at room temperature be no less than about 20, and even more preferably no less than about 100. In another preferred embodiment of the invention, the room temperature vapor pressure of the rinsing agent is preferably from about 0.01 atmosphere (about 8 mm Hg) to about 1 atmosphere (about 760 mm Hg) and even more preferably from about 0.1 (about 80 mm Hg) to about 0.9 atmosphere (about 680 mm Hg). Applicants have found that rinsing agents having vapor pressures within the preferred ranges described above provide the present methods with beneficial characteristics. For example, the preferred methods do not require a prolonged drying step to remove the rinsing agent from the substrate. This advantageous feature is due, at least in part, to the use of high vapor pressure rinsing agents which tend to readily evaporate from the substrate, thereby leaving it clean and dry after the rinsing step. Rinsing agents having the preferred vapor pressure characteristics described herein possess other advantages when used according to the present methods, as described more fully hereinafter.

The present rinsing agents also preferably have little or no known tendency to cause depletion of the ozone layer. More particularly, it is highly preferred that the rinsing agents have an ozone depletion factor (ODP) of no greater than about 0.15, more preferably no greater than about 0.05, and even more preferably of about zero. Ozone depletion factors are reported in Technical Progress On Protecting The Ozone Layer -Electronics, Degreasing and Dry Cleaning Solvents Technical Options Report, United Nations Environment Programme (6/30/89). Rinsing agents consisting of CFC-113, CFC-114 and CFC-115 have ozone depletion



factors of greater than about 0.6 and are therefore not preferred according to the present invention.

As mentioned above and as described in detail below, it is particularly preferred that the solvating and rinsing agents be immiscible with each other. However, for some applications, it is preferred that the rinsing agent be substantially miscible with the solvating agent. According to preferred embodiments described in detail hereinafter, the articles to be cleaned are contacted with a cleaning composition that includes both the solvating agent and the rinsing agent together in the liquid state. In cleaning articles that are fragile and thus subject to being damaged if the composition is agitated unduly, the use of a cleaning composition in which the rinsing agent and the solvating agent are fully miscible in all proportions is desirable because such a composition can be used more effectively with little or no agitation than a composition that includes solvating and rinsing agents which are immiscible with each other.

It should be appreciated by those skilled in the art that the preferred rinsing agents are relatively benign to atmospheric ozone at least in part because of the absence or reduced presence of chlorine in the molecules making up the rinsing agent. However, it will also be appreciated that the reduced chlorine content results in a decrease in the ability of the rinsing agent to solvate many adherent soils, including rosin solder flux. Because of the other features and characteristics of the present invention, however, the relatively low solvating power of the preferred rinsing agents is not detrimental to the cleaning effectiveness of the methods of the present invention. Accordingly, the primary purpose of the present rinsing agents is to wash the solvating agent from the substrate to be cleaned, and it is not required that the rinsing agents have any ability to solvate the adherent soil, although this ability may be present in certain embodiments of the invention.



The rinsing agents of the present invention may also have other desirable and beneficial characteristics. For example, the rinsing agent preferably does not adversely affect the strength, integrity or operability of the materials of construction of the substrate of the components thereof. With respect to substrates comprising a printed circuit board, the rinsing agent is preferably inert with respect to and not a solvent for epoxy resin impregnated fiberglass. The present rinsing agents are also preferably low in toxicity and flammability to improve safety characteristics. It is also highly preferred that the rinsing agents of the present invention are benign to the atmosphere, soil and water. Chemical and photochemical stability are also other preferred features of the rinsing agents. Each of the characteristics noted above with respect to the rinsing agent is equally preferred for the rinsing composition as a whole.

The present rinsing agent is preferably selected from the group consisting of chlorinated hydrocarbons, chlorofluorocarbons, fluorocarbons, hydrofluorocarbons, hydrochlorofluorocarbons, aliphatic hydrocarbons, aromatic hydrocarbons, alcohols, ketones, ethers and mixtures of two or more of the aforementioned. It is even more preferred that the rinsing agent of the present invention be selected from the group consisting of mono- or di-chlorohydrocarbons, mono- or di-chlorofluorocarbons, fluorocarbons, aliphatic hydrocarbons, alcohols and mixtures of two or more of the aforementioned. As the term is used herein, aliphatic hydrocarbon refers to hydrocarbons comprising carbon and hydrogen and includes straight- and branch-chain and cyclic hydrocarbons and saturated and unsaturated hydrocarbons. As the terms are used herein, hydrofluorocarbon and fluorocarbon refer to fluorine-substituted hydrocarbons that do not contain chlorine. The use of perfluorohexane is preferred. Preferred among the alcohols are isopropanol and fluorinated alcohols such as pentafluoropropanol.





Preferred among the hydrochlorofluorocarbons is dichloropentafluoropropane.

A particularly preferred embodiment of the invention comprises the provision of a cleaning composition in which
5 the solvating agent and the rinsing agent are immiscible with each other. The term "immiscible" is used herein in its usual sense to mean that the liquid solvating agent and the liquid rinsing agent do not mix with each other. For example, when the two liquids are brought together, each
10 forms its own layer, with the liquid having the higher specific gravity forming a layer which underlies an overlying layer of the liquid with lower specific gravity. Thus, a composition of this embodiment of the invention, in an undisturbed state, comprises stratified liquid phases.
15 An advantage of the use of immiscible liquids is that the composition in use tends to boil at a relatively constant temperature which is substantially equivalent to the boiling temperature of the rinsing agent alone. In this connection, it is noted that the solvating agent is
20 substantially insoluble in the rinsing agent, and typically, the soil removed from the treated substrate is also substantially insoluble in the rinsing agent - even at the elevated temperatures which may be used to boil the rinsing agent. Inasmuch as the solvating and rinsing
25 agents can be miscible or immiscible with each other, it should be recognized that the present invention includes also within its scope a cleaning composition which comprises solvating and rinsing agents which are partially miscible in each other or partially immiscible with each
30 other.

In a preferred embodiment, the liquid rinsing agent underlies the solvating agent in the stratified form of the composition. In such an embodiment, the relatively high-boiling solvating agent forms a protective cap or blanket
35 over the lower boiling rinsing agent. This deters evaporative loss of the rinsing agent when the composition is not being used. An embodiment of the aforementioned

type of composition can be provided by selecting a rinsing agent which has a higher specific gravity than that of the solvating agent.

5 It is especially preferred that the present rinsing agent be a non-aqueous rinsing agent. As the term is used herein, non-aqueous rinsing agent refers to those rinsing agents which contain only minor amounts, preferably less than five percent and even more preferably less than about one percent, of water. Substantially water-free rinsing
10 agents are especially preferred. While aqueous systems have certain desirable characteristics, such as ready availability and low cost, rinsing agents containing water are frequently corrosive to one or more of the materials of construction of the substrate. Moreover, substrates which
15 are rinsed with water-containing systems are difficult to dry. Thus, the use of water-containing rinsing agents has the detrimental characteristic of being potentially harmful to the substrate being cleaned and/or the components contained therein and of producing substrates which are
20 difficult to dry. Accordingly, the use of rinsing agents or rinsing compositions which contain water is not preferred.

On the other hand, water may be used as a solvating agent in the practice of the present invention inasmuch as water is capable of dissolving many types of soils,
25 including particularly inorganic soils. Water can be used by itself as a solvating agent or in combination with one or more other solvating agents. And it can be used to particular advantage in compositions which comprise immiscible constituents.

30 Excellent results have been achieved in a variety of cleaning applications employing solvating agents and rinsing agents, as described above. There may be, however, applications where improvements in cleaning may be realized by the use of a surfactant(s). Suitable surfactants can be
35 selected based on knowledge in the art.





Many techniques are known and available to those skilled in the art for carrying out the contacting steps of the present invention, and the use of all such techniques is within the scope hereof. Thus, it is generally

5 sufficient that the present contacting steps be carried out under conditions sufficient to achieve the objective of each step. That is, the step of contacting the substrate with a solvating agent preferably proceeds under conditions sufficient to solvate or loosen a predetermined type and

10 amount of adherent soil from the substrate, while the step of contacting the substrate with a rinsing agent preferably proceeds under conditions sufficient to wash a predetermined amount of solvating agent from the substrate. It is contemplated, for example, that the step of

15 contacting the substrate with the solvating agent may include brushing or spraying the substrate with the solvating agent until the predetermined extent of solvation and/or loosening is achieved. Nevertheless, applicants have found that certain effective and beneficial cleaning

20 is achievable according to the preferred contacting conditions described below.

It is generally preferred that the contacting steps of the present invention comprise immersion of the substrate in a liquid or vapor containing the solvating agent and/or

25 the rinsing agent. Furthermore, agitation of the substrate and/or agitation of the contacting medium is also preferred for the purpose of maximizing contact efficiency. In effect, maintaining relative movement between the composition and substrate tends to speed up soil removal.

30 In use, it is highly recommended, and thus particularly preferred, that a composition comprising immiscible liquids be agitated. Agitation of the immiscible constituents of the composition results in the formation of a mixture thereof and causes the rinsing agent to be moved toward and

35 to the surface of the heated composition where it vaporizes. The composition tends to boil more uniformly. Upon termination of the cleaning process, including terminating agitation of the composition, the immiscible



liquids separate readily into two distinct layers as the composition cools below the boiling point of the rinsing agent. The soil removed from the treated part collects typically in the layer of solvating agent. Thus,
5 contamination of the rinsing agent with soil can be avoided.

Also, in practice, the system may not have a flash point even if operated above the flash point of the high boiling agent. This will occur because the low boiler can
10 be chosen to not have a flash point and in operation the low boiler will fill the equipment system with a non-combustible vapor phase.

With respect to the sequence of the contacting steps, it is contemplated that the step of contacting the
15 substrate with the rinsing agent may be carried out substantially simultaneously with and/or subsequent to the step of contacting the substrate with the liquid solvating agent, subsequent contact being preferred according to certain embodiments.

20 The duration of the contacting steps of the present invention also may vary widely, depending upon a number of factors, such as the type and nature of the adherent soil, the materials of construction of the substrate and the extent of cleaning desired, and all such durations are
25 within the scope of the present invention. Preferably, however, the step of contacting the substrate with solvating agent comprises maintaining the substrate in contact with the solvating agent for a time sufficient to solvate or at least loosen substantially all of the
30 adherent soil from the substrate. It is contemplated that a person of ordinary skill in the art, with the guidance provided by the present disclosure, will be readily able to determine the appropriate contact time for any particular application without undue experimentation. It is
35 especially preferred, however, that the substrate be contacted with the solvating agent for a period of from



about 30 seconds to about 5 minutes, and even more preferably from about 30 seconds to about 2 minutes.

The step of contacting the substrate with rinsing agent preferably comprises contacting the substrate with
5 rinsing agent for a period of time effective to wash from the substrate a major proportion, and preferably substantially all, of the solvating agent. Once again, it is contemplated that one of ordinary skill in the art, with the guidance provided by the present application, will be
10 readily able to determine the exact contact time required for any specific application without undue experimentation. It is generally preferred, however, that the substrate be contacted with the rinsing agent for a period of from about 30 seconds to about 5 minutes, and even more preferably
15 from about 30 seconds to about 3 minutes.

The use of contacting steps according to the duration periods described above are especially preferred for methods which comprise the removal of rosin solder flux from printed circuit boards, especially such methods which
20 utilize a rinsing agent comprising chlorofluorocarbons, hydrochlorofluorocarbons, fluorocarbons or alcohols, and a solvating agent comprising a terpene or terpene-based material, or ester or ester-based material, for example, a monobasic or dibasic ester, the former being preferred.

25 The temperature and pressure conditions under which the contacting steps are carried out may also vary widely, depending upon numerous factors, such as the cost and availability of heating and cooling mediums, and all such variations are within the scope of the present invention.
30 For the purposes of simplicity, it is generally preferred that the contacting steps be carried out at about ambient pressure conditions. With respect to temperature conditions, it is highly preferred that the step of contacting the substrate with a solvating agent comprise:
35 (1) providing a solvating agent at a temperature of from about 10°C (about 50°F) to about 150°C (about 300°F), and



even more preferably of from about 30°C (about 80°F) to about 120°C (about 250°F); and (2) contacting the substrate with provided solvating agent. It is also preferred that the invention comprise contacting the substrate with a boiling liquid comprising solvating agent, especially when such boiling occurs within the temperature ranges described above.

According to one preferred embodiment of the invention, the step of contacting the substrate with rinsing agent comprises contacting the substrate with vapor comprising rinsing agent, the temperature of the substrate being less than about the temperature of the vapor, preferably at least about 5 C° less than the temperature of the vapor. It is further preferred that the step of contacting the substrate with a rinsing agent comprises: (1) providing a rinsing agent at a temperature of from about 5°C (about 40°F) to about 120°C (about 250°F), and even more preferably from about 20°C (about 70°F) to about 100°C (about 230°F); and (2) contacting the substrate with the provided rinsing agent. Applicants have found that the effectiveness of the solvating and rinsing steps of the present invention is substantially improved when carried out under the temperature conditions described above.

With respect to the actual contact mechanism, it is contemplated that all known contacting techniques are adaptable for use according to the present methods. Thus, for the liquid solvating and rinsing agents, the contacting step may comprise, for example, spraying, brushing and/or immersing of the substrate, with immersion being preferred. For rinsing agents in the vapor state, the contacting step may comprise, for example, blowing rinsing agent vapors across the substrate and/or immersing the substrate in rinsing agent vapors, with immersion being preferred.

An especially preferred embodiment of the present methods comprises: (a) contacting the substrate with a boiling liquid composition comprising solvating agent and



rinsing agent; and (b) contacting the substrate with a vapor comprising a major proportion by volume of rinsing agent and a minor proportion by volume of solvating agent, the ratio of the vapor pressure of said rinsing agent to the vapor pressure of said solvating agent being at least about 20. It has been found that this embodiment is highly preferred because it permits a simplified yet effective process design. According to certain embodiments, the use of a boiling liquid containing solvating agent establishes the preferred elevated temperature contact between the substrate and the solvating agent. Furthermore, the provision of a boiling liquid comprising a low vapor pressure solvating component and a high vapor pressure rinsing component results in the generation of a vapor space above the boiling liquid which comprises rinsing agent in major proportion and only minor amounts, if any, of solvating agent. Thus, the effective elimination of solvating agent from the vapor space coupled with the close proximity of the boiling liquid to the vaporous rinsing agent allows a simple and highly effective process design. In its most preferred form, the solvating and rinsing agents are immiscible with each other.

With particular reference now to FIG. 1, a batch mode cleaning process according to one embodiment of the present invention is illustrated. The methods according to this embodiment utilize a partitioned cleaning tank 10 having a first section 11 and a second section 12 separated by a partitioning member or weir 13. The first section 11 of tank 10 is filled to a first, predefined level with a liquid cleaning composition 14 comprising solvating agent, and the second section 12 is filled to a second predefined level above said first predefined level with a liquid rinsing composition 15 comprising rinsing agent. Condensing coils 16 are provided in the vapor space above the liquids contained in tank 10. The first section 11 of tank 10 is provided with heating coils 18 for adding heat to the liquid cleaning composition, and the second section 15 of tank 10 is provided with cooling coils 20 for



removing heat from the liquid cleaning composition. For
embodiments of the type illustrated in FIG. 1, it is
especially preferred that the liquid cleaning composition
14 contained in the first tank section 11 comprise
5 solvating agent and rinsing agent, with the solvating agent
preferably being present in major proportion, preferably
about 50 to about 80 percent by weight of the liquid
cleaning composition, and the rinsing agent preferably
being present in minor proportion, preferably from about 20
10 to about 40 weight percent of the liquid cleaning
composition. Heating element 18 is preferably controlled
to raise the temperature of the liquid cleaning composition
to about the boiling point.

Overlying the liquids contained in section 11 and 12
15 of the cleaning tank is a vapor 19 which comprises the
rinsing agent of the present invention. More particularly,
as the temperature in tank section 11 is raised to the
boiling point of the liquid cleaning composition 14, the
rinsing agent contained therein is preferentially vaporized
20 and fills the vapor space 19 of the cleaning tank 10.
Coolant flow through condensing coil 16 is regulated so as
to condense about the same amount of vapor as is produced
by the boiling liquid contained in first tank section 11.
Condensed liquid transfer means (not shown) deliver the
25 condensed liquid into the second section 12 of tank 10.
The proper level of cool, rinsing agent contained in the
second tank section 12 is controlled by the height of
partition member or overflow weir 13. Excess liquid
rinsing agent flows over weir 13 and into the first tank
30 section 11, thereby replenishing rinsing agent lost
therefrom by vaporization.

One preferred embodiment of the present methods will
now be described in connection with the use of the
apparatus illustrated in FIG. 1 to clean a printed circuit
35 board containing residual rosin solder flux. The first
step comprises contacting the contaminated printed circuit
board with solvating agent by immersing the board in the



boiling liquid contained in first section 11 of tank 10, thereby solvating and/or loosening any residual rosin flux present on the board. The first contacting step preferably has a duration of about 1 to about 7 minutes. The next
5 step comprises contacting the printed circuit board with rinsing agent so as to wash solvating agent, and any rosin flux dissolved therein or loosened thereby, from the circuit board. This second contacting step preferably comprises conducting two or more of the following steps
10 substantially sequentially: (i) contacting the printed circuit board with rinsing agent by subjecting the board to the vapor space 19 overlying the liquid tank 10 substantially immediately upon removal of the board from contact with the solvating agent; (ii) further contacting
15 the printed circuit board with rinsing agent by immersing the board in the relatively cool liquid rinsing agent contained in the second section of the tank 10; and (iii) further contacting the printed circuit board with rinsing agent by immersing the printed circuit board in the vapor
20 space 19 overlying the liquid tank 10. This preferred sequence of contacting steps is believed to provide a highly effective technique for cleaning and drying substrates containing adherent soil.

The contacting step (i) described above is
25 advantageous because it permits excess solvating agent and associated soil to be washed off the board and returned under the influence of gravity to the boiling liquid. Thus, contamination of the rinsing liquid contained in section 12 of tank 10 with solvating agent and/or removed
30 soil is minimized. It is contemplated that for certain embodiments, contacting step (i) will provide acceptably clean and dry printed circuit boards. For more stringent requirements, however, it is preferred that the further contacting steps (ii) and (iii) be utilized. In
35 particular, the printed circuit board is preferably removed from the vapor space above tank section 11 and immersed in the relatively cool rinsing composition contained in tank section 12. This further contacting step provides



additional rinsing and also serves to cool the board, preferably to about the temperature of the liquid in tank section 12. The final step in this preferred embodiment comprises removing the printed circuit board from the cool
5 rinsing liquid and contacting the printed circuit board once again with the relatively hot vapor contained in the vapor space 19. Because of the temperature differential, the rinsing agent in the vapor space will condense on the substrate, thereby providing a final rinse step and a
10 clean, dry printed circuit board.

EXAMPLES

The following examples are illustrative and/or comparative but not limiting of the present invention. The designation of examples as comparative is not necessarily
15 an indication that the examples represent prior art procedures.

EXAMPLE 1

About 270 parts by weight (pbw) of a rinsing agent consisting of 1,1,1-trichloroethane and about 630 pbw of a
20 solvating agent consisting of limonene were combined in a heated vessel to form a liquid cleaning composition consisting of about 70 percent by weight of limonene solvating agent and about 30 percent by weight of 1,1,1-trichloroethane rinsing agent. The liquid cleaner
25 contained in the heated vessel was then brought to a boil, at which time the temperature of the liquid was about 140°C. The vapor space immediately overlying the boiling liquid consisted essentially of 1,1,1-trichloroethane and only trace amounts of limonene. Due primarily to heat loss
30 through the uninsulated wall of the vessel, the temperature of the vapor space was about 66 C° below the temperature of the boiling liquid.

A 1" x 2" rectangular metal test coupon having a thickness of about one-sixteenth of an inch was



contaminated at about room temperature with cutting oil. The contaminated coupon was then placed in the vapor space above the boiling liquid, whereupon the 1,1,1-trichloroethane vapor contacted the coupon and condensed thereon. The coupon was held in the vapor space until the temperature of the coupon equilibrated with the temperature of the vapor space, as evidenced by a cessation of condensation forming on the coupon. The coupon was removed from the vapor, observed and found to be contaminated with cutting oil, thereby indicating that the step of contacting the coupon with vaporous rinsing agent was alone not sufficient to remove the substantially all of the contaminant from the coupon.

The still contaminated coupon was then contacted with limonene solvating agent by immersing the coupon in the boiling liquid for a time sufficient to solvate or loosen substantially all of the contaminant, that is about 45-60 seconds. The coupon was then removed from the boiling liquid and placed in a vessel containing liquid 1,1,1-trichloroethane at about room temperature for time sufficient to allow the coupon to be cooled to about room temperature, that is, about 60 seconds. Further contact with the rinsing agent was then achieved by again immersing the coupon in the vapor space immediately above the boiling liquid for a time sufficient to observe cessation of condensation on the coupon, that is, about 40 - 60 seconds, thereby contacting the coupon with a vapor consisting essentially of the rinsing agent 1,1,1-trichloroethane. The coupon was again removed from the vapor and found to be substantially dry and free of cutting oil contaminant and solvating agent.

EXAMPLE 2

An apparatus of the general type illustrated in FIG. 1 was utilized to remove asphalt contaminant from a wire rod coated therewith, except that cooling coils 20 were not provided in the second section 12 of the vessel. A



cleaning composition was prepared by combining about 270 parts by weight (pbw) of a rinsing agent consisting of isopropanol and about 630 pbw of a solvating agent consisting of limonene. The first section of the apparatus
5 was charged with the liquid cleaning composition and the second section of the apparatus was charged with a liquid consisting essentially of isopropanol. The liquid cleaning composition was heated until boiling occurred. The temperature of the boiling cleaning liquid was about 92°C.
10 The vapors rising from the boiling liquid were condensed and transferred to the second section of the apparatus at a rate sufficient to maintain a substantially constant liquid level in both the first and second sections thereof. The vapor space immediately overlying the boiling liquid
15 consisted essentially of isopropanol and only trace amounts of limonene. Due primarily to heat loss through the uninsulated wall of the vessel, the temperature of the vapor space was about 9 C° below the temperature of the boiling liquid. The liquid in the second section of the
20 tank was at a temperature of about 25 - 40°C and consisted essentially of isopropanol and only trace amounts of limonene.

A wire rod was coated with asphalt and then allowed to cool to about room temperature. The contaminated rod was
25 then placed into the vapor space immediately above the boiling liquid for a time period sufficient to allow substantial cessation of condensation of the vapors on the rod, that is, about 40 - 60 seconds. The wire rod was then removed from the vapor space, observed and found to remain
30 substantially contaminated with the asphalt. The wire rod was then passed through the vapor space and placed into the boiling liquid. The wire rod was held in the boiling liquid for about 60 seconds. Upon removal from the boiling liquid, the wire rod was found to be substantially free of
35 asphalt, but wet with solvating agent.

The clean but wet wire rod was then immersed in the cool liquid rinsing agent for about 60 seconds. The rod



was then placed in the vapor phase above the boiling liquid for a period sufficient to observe a cessation of condensation on the wire rod, that is, about 40 - 60 seconds. The wire rod was then again removed from the vapor and found to be both clean and dry.

EXAMPLE 3

Example 2 was repeated, except that the contaminant was a high melting temperature wax. The wire rod was coated by dipping in molten wax and then allowed to cool to about room temperature. The coated wire rod was then placed into the vapor space immediately above the boiling liquid for a time period sufficient to allow a substantial reduction in the rate of condensation of the vapors on the rod, that is, about 20 - 30 seconds. The wire rod was then removed from the vapor space, observed and found to remain substantially contaminated with the wax, although softening of the wax had apparently occurred. The wire rod was allowed to cool and was then immersed in the boiling liquid for about 60 seconds. Upon removal from the boiling liquid, the coated wire rod was found to be substantially free of wax but wet with solvating agent.

The clean but wet wire rod was then immersed in the cool liquid rinsing agent for about 10 - 20 seconds. The rod was then immersed in the vapor phase above the boiling liquid for a period sufficient to observe a cessation of condensation on the wire rod, that is, about 40 - 60 seconds. The wire rod was then again removed from the vapor and found to be both clean and dry.

EXAMPLE 4

An apparatus of the general type illustrated in FIG. 1 was utilized to remove Boscan crude oil from a wire rod coated therewith, except that the second section of the apparatus was not charged with rinsing liquid and condensed vapors were returned directly to the boiling cleaning



liquid. The first section of the apparatus was charged with the liquid cleaning composition of Example 2. The liquid cleaning composition was heated until boiling occurred. The temperature of the boiling cleaning liquid was about 92°C. The vapors rising from the boiling liquid were condensed and returned to the boiling liquid. The vapor space immediately overlying the boiling liquid consisted essentially of isopropanol and only trace amounts of limonene. Due primarily to heat loss throughout the uninsulated wall of the vessel, the temperature of the vapor space was about 17 C° below the temperature of the boiling liquid.

A wire rod was coated with Boscan crude oil and allowed to cool to room temperature. The contaminated rod was then placed into the vapor space immediately above the boiling liquid for a time period sufficient to allow substantial cessation of condensation of the vapors on the rod, that is, about 40 -60 seconds. A few drops of oil were then observed to fall from the contaminated wire hanger. The wire rod was then removed from the vapor space, observed and found to remain substantially contaminated with the crude oil. The wire rod was then immersed in the boiling liquid for about 30 seconds and then raised into the vapor space immediately above the boiling liquid. The wire rod was then held in the vapor space for a period of about 30 seconds, after which it was withdrawn from the apparatus and allowed to cool. The wire rod was observed to be substantially clean but slightly damp. The wire rod was then reimmersed in the vapor phase above the boiling liquid for a period sufficient to observe a cessation of condensation on the wire rod, that is, about 40 - 60 seconds. The wire rod was then again removed from the vapor and found to be both clean and dry.

EXAMPLE 5

An apparatus of the general type illustrated in FIG. 1 was utilized to clean a polyamide resin contaminant from a



wire rod coated therewith. A cleaning solution was prepared by combining about 270 pbw of a rinsing agent consisting of 1,1,1-trichloroethane and about 630 pbw of a solvating agent consisting of limonene. The first section
5 of the apparatus was charged with the liquid cleaning composition and the second section of the apparatus was charged with a liquid consisting essentially of 1,1,1-trichloroethane. Heat was applied to the liquid until boiling occurred. The vapors rising from the boiling
10 liquid were condensed and transferred to the second section of the apparatus at a rate sufficient to maintain a substantially constant liquid level in both the first and second sections thereof. The temperature of the boiling liquid was about 118°C, and the temperature of the cool
15 liquid in the second section of the tank was about 25 - 40°C. Due primarily to heat loss through the uninsulated wall of the vessel, the temperature of the vapor space was about 44 C° below the temperature of the boiling liquid. The vapor directly above the boiling liquid consisted
20 essentially of 1,1,1-trichloroethane, with no more than trace amounts of limonene present.

A wire rod was coated by dipping in molten polyamide residue available from Union Camp under the designation
25 UNI-REZ 2646 and then allowed to cool to about room temperature. The contaminated wire rod was then placed in the vapor space above the boiling liquid, whereupon the 1,1,1-trichloroethane vapor contacted the rod and condensed thereon. The wire rod was held in the vapor space for
30 about one minute and then removed. No removal of contaminant from the rod was evident, thereby indicating that the step of contacting the wire rod with vaporous rinsing agent was alone not sufficient to remove the contaminant from the wire rod.

35 The still contaminated wire rod was then contacted with limonene solvating agent by immersing the rod in the boiling liquid for a time sufficient to solvate or loosen



substantially all of the contaminant, that is, about six minutes. The wire rod was then removed from the boiling liquid and placed in the section of the apparatus containing the cool liquid 1,1,1-trichloroethane for about 5 60 seconds. Further contact with the rinsing agent was then achieved by again placing the rod in the vapor space immediately above the boiling liquid for a time sufficient to observe a substantial reduction in the rate of condensation on the rod, that is, about 40 - 60 seconds, 10 thereby contacting the rod with a vapor consisting essentially of the rinsing agent 1,1,1-trichloroethane. The rod was again removed from the vapor and found to be substantially dry and free of resin contaminant and solvating agent.

15 The next group of examples (Examples 6 to 9 inclusive) illustrates the use of compositions which are within the scope of the present invention and which include solvating agents and rinsing agents which are immiscible with each other. The rinsing agent which was used in the composition 20 of these examples is perfluorohexane (C_6F_{14}). Table 1 below contains information respecting various of the physical properties of perfluorohexane.

Table 1

Properties of Perfluorohexane

25	Basic Formula	C_6F_{14}
	Flash Point, °C	None
	Normal Boiling Point, °C	56
	Pour Point, °C	-90
30	Liquid Density, 25°C, gm/ml	1.68
	Liquid Viscosity, 25°C, cp	0.67
	Vapor Pressure, 25°C, mm Hg	232
	Thermal Conductivity, w/(cm)(°C) x 10 ³	0.57
	Specific heat, 25°C, cal/(gm)(°C)	0.25
35	Heat of Vaporization @ b.P cal/gm	21
	Coefficient of Thermal Expansion, 25°C ml/(ml)(°C) x 10 ³	1.6
	Surface Tension, 25°C, dynes/cm	12
	Solubility of Water, 25°C, dynes/ppm	10
40	Ozone Depletion Potential (ODP)	zero

EXAMPLE 6

The composition of this example comprised 50 wt.% of isopropyl myristate (solvating agent) and 50 wt.% of perfluorohexane (rinsing agent). The individual components
5 were placed in a vessel which was equipped with a stirrer and heater and to which a condenser was attached. The components were stirred to form a mixture which was heated to boiling to produce a steady reflux of the rinsing agent. A metal part was coated with a cutting oil and immersed for
10 1 to 2 minutes in the boiling composition which had a temperature of 138°F (about 59°C). The part was then withdrawn from the composition and raised above the vapor zone of the apparatus where it was allowed to cool to about room temperature. The cooled part was then lowered to the
15 vapor zone where vapor of perfluorohexane condensed on the cooled part. The temperature of the vapor in the vapor zone was 136°F which is the same temperature as the boiling temperature of perfluorohexane. The part was kept in the vapor of the vapor zone for 5 to 7 minutes at which time
20 liquid had stopped condensing on the part. The part was removed from the vapor zone and ascertained to be clean and dry.

EXAMPLE 7

There was added to the composition of Example 6 an
25 amount of cutting oil such that the composition contained 15 wt.% of oil (based on the total weight of the composition). The procedure described in Example 6 was re-run utilizing the composition with added oil. The results obtained were the same as those reported in Example 6 in
30 terms of cleaning and drying. The temperatures of the boiling composition and of the vapor were also the same as those reported in Example 6. When the agitation and input of heat were terminated, the composition separated into two distinct layers. It was observed that the bottom layer
35 consisted of the perfluorohexane which has a higher



specific gravity than isopropyl myristate. The layer of perfluorohexane was clear and apparently uncontaminated with soil or cleaner. The upper layer of the composition comprised the isopropyl myristate which showed the distinct
5 color of the cutting oil.

EXAMPLE 8

The procedures described in Examples 6 and 7 above were re-run except that methyl caprate was substituted for isopropyl myristate. The results obtained were the same as
10 those reported in Examples 6 and 7.

EXAMPLE 9

The procedures described in Examples 6 to 8 above were repeated, except that the compositions were modified by including therein about 10 ppm of a non-ionic fluoro liquid
15 surfactant sold by 3M Company under the trademark Fluorad FC-430 and characterized by 3M Company as fluoroaliphatic polymeric esters.

The cleaning results were the same as those described in Examples 6 to 8.

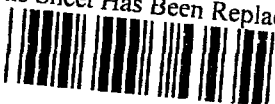
20

COMPARATIVE EXAMPLE A

A rinsing agent consisting of isopropanol was charged to a heated vessel at about atmospheric pressure and brought to a boil.

25 A wire rod was coated with asphalt and allowed to cool to about room temperature. The contaminated rod was immersed in the boiling liquid for about 60 seconds. Upon removal from the boiling liquid, no removal of asphalt from the rod was evident.

30 Another example of the practice of the present invention involved the use of a cleaning composition which



comprised "immiscible" solvating and rinsing agents and which was used in a commercially available cleaner that was modified in the manner described below. The cleaning composition comprised 80 wt% of solvating agent and 20 wt% of rinsing agent. The solvating agent was a terpene-based composition that was comprised predominately of *d*-limonene and that is sold under the trademark BIOACT 121 by Petroferm Inc. The rinsing agent was perfluorohexane. The cleaner that was used was an electrically heated, water cooled piece of equipment sold by Detrex Chemical Industries, Inc., as model 2D 12-EW solvent cleaner (hereafter "the Detrex cleaner"). The Detrex cleaner has a compartment for holding and heating the cleaning composition comprising the solvating and rinsing agents and a compartment for holding the rinsing agent. The Detrex cleaner was modified to include means for agitating the cleaning composition and the rinsing composition, such means consisting of a pump which withdrew the cleaning composition from the bottom of the compartment in which it was held and which pumped the cleaning composition back into the main body thereof through nozzles. The compartment holding the rinsing agent was modified in the same way to achieve agitation of the body of rinsing agent in the compartment holding it. The Detrex cleaner comes equipped with a vapor zone that includes cooling coils. The Detrex cleaner was modified to include an additional set of cooling coils that were placed above the original equipment coils and which were cooled to -20°F by means of a refrigerating system. The additional cooling coils were used to minimize evaporative losses of the rinsing agent. It should be appreciated that the present invention can be used effectively with other types of cleaning equipment that are available commercially or that can be modified readily to accommodate the practice of the present invention.



What is claimed is:

1. A process for removing rosin solder flux from a printed circuit board comprising:

5 (a) contacting the printed circuit board with a boiling liquid comprising solvating agent and rinsing agent, said solvating agent having:

(i) a room temperature vapor pressure of no greater than about 10 mm Hg; and
10 (ii) a solvating strength of no less than about 10,

and said rinsing agent having:

(i) a room temperature vapor pressure of from about 80 mm Hg to about 760 mm Hg and an ozone depleting factor of from about 0 to
15 about 0.05;

(b) subsequent to step (a), contacting the substrate with a cool liquid comprising said rinsing agent and having a temperature at least about 5 C° below the temperature of said boiling liquid;

20 (c) allowing the contacting step (b) to continue for a time sufficient to reduce the temperature of said substrate to about the temperature of said liquid;

(d) subsequent to step (c), contacting the substrate with a vapor consisting essentially of said rinsing agent and having a temperature at least about 5 C°
25 above the temperature of said cool liquid; and

(e) allowing the contacting step of step (d) to continue for a time sufficient to increase the temperature of said substrate to about the temperature
30 of said vapor.

2. The process of Claim 1 wherein said boiling liquid comprises a major proportion by weight of solvating agent.

3. The process of Claim 1 wherein the solvating
35 agent is selected from the group consisting of terpenes, terpene-based compounds and mixtures of these.





4. The process of Claim 1 wherein said rinsing agent is selected from the group consisting of chlorinated hydrocarbons, chlorofluorocarbons, fluorocarbons, hydrofluorocarbons, hydrochlorofluorocarbons, alcohols, 5 fluorinated alcohols, and mixtures of these.

5. The process of Claim 1 wherein said solvating agent consists essentially of terpene and said rinsing agent consists essentially of fluorocarbon.

6. The process of Claim 5 wherein said rinsing agent 10 consists essentially of perfluorohexane.

7. The process of Claim 1 wherein the solvating agent consists essentially of one or more organic esters.

8. A process for removing adherent soil from a printed circuit board comprising:

- 15 (a) contacting the printed circuit board with a cleaning liquid comprising solvating agent and rinsing agent, the ratio of the vapor pressure of said rinsing agent to the vapor pressure of said solvating agent being at least about 20, and said 20 rinsing agent having an ozone depletion factor of no greater than about 0.15; and
- (b) subsequent to (a), contacting the substrate with a rinsing composition substantially free of said solvating agent in major proportion.

25 9. The process of Claim 8 wherein said cleaning liquid is a boiling liquid.

10. A process for removing soil from a substrate comprising:

- 30 (a) contacting the substrate with a liquid cleaning composition comprising a solvating agent; and
- (b) contacting the substrate with a rinsing agent, the temperature of said rinsing agent





5

being at least 5 C° below the temperature of said liquid solvating agent, the ratio of the vapor pressure of said rinsing agent to the vapor pressure of said solvating agent being at least about 20.

11. The process of Claim 10 wherein said liquid cleaning composition comprises said solvating agent and said rinsing agent and including heating said composition to boil said rinsing agent.

10

12. The process of Claim 11 wherein said solvating agent consists essentially of terpene or organic ester and said rinsing agent is selected from the group consisting of chlorofluorocarbons, fluorocarbons, hydrofluorocarbons, hydrochlorofluorocarbons, alcohols, fluorinated alcohols, and mixtures of these.

15

13. A liquid composition comprising solvating agent and rinsing agent, said solvating agent having:

20

- (i) a room temperature vapor pressure of no greater than about 10 mm Hg; and
- (ii) a solvating strength of no less than about 10,

and said rinsing agent having:

25

- (i) a room temperature vapor pressure of from about 80 mm Hg to about 760 mm Hg and an ozone depleting factor of from about 0 to about 0.05.

14. The composition of Claim 13 wherein said composition comprises a major proportion by weight of solvating agent.

30

15. The composition of Claim 13 wherein the solvating agent is selected from the group consisting of terpenes, terpene-based compounds and mixtures of these.





16. The composition of Claim 13 wherein said rinsing agent is selected from the group consisting of chlorinated hydrocarbons, chlorofluorocarbons, fluorocarbons, hydrofluorocarbons, hydrochlorofluorocarbons, alcohols, fluorinated alcohols and mixtures of these.

17. A composition comprising a solvating agent and a rinsing agent that are immiscible with each other and wherein the ratio of the vapor pressure of said rinsing agent to the vapor pressure of said solvating agent is at least about 20.

18. A composition according to Claim 17 wherein said rinsing agent has an ozone depletion factor of no greater than about 0.15.

19. A composition according to Claim 17 wherein said solvating agent consists essentially of a terpene and said rinsing agent consists essentially of a fluorocarbon or a hydrofluorocarbon.

20. A composition according to Claim 17 wherein said solvating agent consists essentially of an organic ester and said rinsing agent consists essentially of a fluorocarbon or a hydrofluorocarbon.

21. A process according to Claim 1, 8, or 10 wherein said solvating agent and said rinsing agent are immiscible with each other.

22. A composition according to Claim 13 or 17 wherein said solvating agent and said rinsing agent are immiscible with each other.

23. A process according to Claim 21 including agitating said liquid.

24. In a cleaning apparatus which includes means for holding a cleaning composition, means for heating said





cleaning composition, and means for holding a rinsing
agent, and which includes also a vapor zone overlying said
cleaning composition and cooling means for condensing vapor
in said vapor zone, the improvement comprising means for
5 agitating said cleaning composition and means for agitating
said rinsing agent.

