

LOW-RESIDUE ROSIN-FREE SOLDERING FLUX

This invention relates to a low-residue rosin-free soldering flux, especially a flux containing a dibasic acid mixture, that, in use, is essentially non-corrosive and ionic residue-free.

5 A soldering flux is used to aid fusion of metal parts being joined together by soldering, by reacting with and dissolving the surface oxides or impurities thereon whilst coating the surfaces against oxidation, during soldering at a temperature above the
10 solder melting point.

Organic fluxes are typically based on water-insoluble rosin or a water-soluble organic acid. Activated rosin fluxes are used in soldering electrical connections on printed circuit boards. Wave-soldering
15 is used for mass production circuit board soldering as by applying the flux, pre-heating the board, applying the solder (e.g., via a molten solder standing wave), cooling the board, and cleaning it to remove flux residue therefrom.

20 Such flux residue is mainly constituted of ionic (e.g., acidic or basic) substances, and is corrosive, or can hydrolyze to corrosive constituents in the presence of moisture (e.g., air moisture). This can lead to short-circuits, noise generation, etc., in
25 use of the circuit board product. These adverse results are effectively avoided by subjecting the soldered board to a cleaning step to remove the ionic substances therefrom.

U.S. Patent No. 2,715,084 (Konig) shows a
30 flux of rosin activated by a chain-brominated higher aliphatic monocarboxylic acid or salt of 8-24 chain carbon atoms (e.g., alpha-bromolauric acid), in turpentine, that does not decompose at the soldering temperature. It is non-corrosive as the chain bromine

is not ionic so that the compound does not hydrolyze to a corrosive halide, as with acid or halide salt flux, or rosin flux activated by organic base halide (e.g., cetyl-pyridinium halide), wherein the halide as an anion can hydrolyze in air to form a corrosive acid halide. Brominated acids of less than 8 carbon atoms are excluded as being corrosive and of less surface activity.

U.S. Patent No. 2,898,255 (Thompson et al.) shows a non-corrosive printed circuit board flux of rosin activated by a combination of both an aliphatic monocarboxylic acid (e.g., formic, acetic or propionic acid) and an aliphatic dicarboxylic acid (e.g., oxalic, malonic, succinic, glutaric or adipic acid), in isopropanol, that does not splatter during soldering. The sole example given of a non-splattering flux is a mixture of rosin (mp 120°C/248°F), formic acid (bp 100°C/212.5°F) and glutaric acid (bp 200°C/392°F), in isopropyl alcohol, in which the low glutaric acid content (about 1%) is said to prevent splattering, whilst the given melting and boiling points of the components are said to permit step-by-step de-oxidation of the oxide surface being soldered.

U.S. Patent No. 2,904,459 (Kubota) shows a liquid, paste or solid flux for electrical application. The flux is based on rosin converted to pure, stable abietic acid amine salt (e.g., diethylene amine salt), that is insoluble and does not hydrolyze, and whose neutral resinous residue on soldering is non-corrosive and non-hygroscopic, unlike commercial rosin which, besides a 25-30% content of abietic acid (i.e., a monobasic organic acid), that has fluxing action, also has a resinous remainder that can cause soldered product defects.

U.S. Patent Nos. 3,235,414 (Marks) and 3,264,146 (Marks) show a rosin-free food can soldering flux. It is formed as a relatively concentrated solution of a large percentage (e.g., 25 wt. parts) of an aliphatic dicarboxylic acid of 9-10 carbon atoms with at least 4 carbon atoms in the chain separating the carboxyl groups (e.g., azelaic or sebacic acid), or its anhydride or ester, that is modified by (e.g., 1.2 wt. parts) ethanolamine hydrochloride, in (e.g., 75 wt. parts) dimethylformamide as polar solvent. Such acids with 3 or less carbon atoms separating the carboxyl groups present in the molecule are undesired in forming monoanhydrides from a single molecule.

U.S. Patent No. 3,837,932 (Aronberg) shows a 10-80% polycarboxylic acid particulate suspension (e.g., adipic acid), in an aqueous solution of 0.2-5% soluble gum (remainder 15-89.8% water), as a rosin-free soldering flux for bonding lead storage battery plate lugs to straps, in which the acid (e.g., adipic) does not sublime at the high (482°C/900°F) bonding temperature used. Use of the dry particulate acid alone, applied to the lugs after pre-heating, is less preferred.

U.S. Patent No. 4,168,996 (Zado) shows a mixture of rosin, an activator with both a halogen and a destabilizing substituent, such a halogenated mono or dibasic organic acid (e.g., 2,3-dibromosuccinic acid), and a solder surfactant such as a polycarboxylic acid (e.g., adipic, sebacic or azelaic acid), or hydroxyl substituted polybasic acid, and/or keto acid (e.g., levulinic acid), in ethanol or isopropyl alcohol, and optionally a secondary activator (e.g., diethylamine hydrochloride) and a non-ionic foaming agent, as being activated rosin flux of synergistic effect for

the soldering of printed circuit boards.

Zado notes that using rosin with the activator or solder surfactant alone does not provide the synergistic effect, and that the combination acid containing rosin flux of the above-discussed U.S. patent 2,898,255 is too acidic and corrosive for practical use in electronics soldering.

The importance of a residue-free soldered connection is discussed in the article entitled: "Europeans find ways to phase-out CFCs," Electronic Packaging & Production, Vol. 29, No. 1, Jan. 1989, pp. 26 and 28, Linda Smith-Vargo, Associate Editor. The article notes that fluxes used in printed circuit board applications leave residues that must be cleaned, typically by using an organic liquid based on fully halogenated chlorofluorocarbons or CFCs, but that in view of the need to reduce CFC emissions, due to environmental constraints, soldering procedures are needed that avoid CFCs yet produce a residue-free non-corrosive product.

It is desirable to have a flux for soldering metal connections in electrical applications such as printed circuit boards that does not produce a corrosion-causing and/or hydrolyzable ionic residue that requires a cleaning step for its removal.

This invention solves the foregoing problems by providing a low-residue soldering flux and, particularly, a flux containing a dibasic acid mixture or three-acid mixture (TAM) that in use is essentially non-corrosive and ionic residue-free.

All percentages (%), parts (pts) or proportions set forth herein are by weight unless specifically indicated otherwise.

A low-residue organic soldering flux in

accordance with the present invention consists of a rosin-free, essentially non-subliming dibasic acid mixture of succinic, glutaric and adipic acids having a melting point of 90-130°C and a boiling point of 150-210°C in a dilute solution in a volatilizable organic solvent, said mixture being capable of essentially completely volatilizing during use as a flux on a soldering site during heat-soldering of said soldering site, so as to leave the soldering site essentially free from any ionic residue from the flux.

The low-residue flux of the invention is used in heat-soldering metal components, and the three-acid mixture is an essentially non-subliming dibasic acid mixture of succinic, glutaric and adipic acids. It especially contains about 15-30% succinic acid, 40-63% glutaric acid and 10-30% adipic acid and, more particularly, about 18-30% succinic acid, 51-61% glutaric acid and 11-30% adipic acid. The percentages of succinic, glutaric and adipic acid are based on the total dibasic acid mixture.

The three-acid mixture has a melting point (mp) of 90-130°C and a boiling point (bp) of 150-210°C, especially 170-195°C, and is capable of essentially completely volatilizing during heat-soldering to leave the soldered site essentially free from ionic residue. In particular, it is capable of leaving at most a trace amount of a residue of corrosive, or hydrolyzable potentially corrosive, ionic (e.g., acidic) constituents.

The soldered site such as an electronic circuit board needs no cleaning to remove the ionic residue (e.g., by chlorofluorocarbons or like environmentally-objectionable washing liquids), and may be further processed without a cleaning step.

As used herein, essentially "non-subliming" means that the constituents of the three-acid mixture in the flux that volatilize during the heat-soldering operation, remain volatilized and do not re-condense and/or re-deposit at the soldering site as ionic residue. Thus, the three-acid mixture is an essentially non-re-condensing and non-re-depositing volatilizable dibasic acid mixture according to the invention.

10 The flux is a rosin-free flux comprising said three-acid mixture.

The rosin-free flux comprises a rosin-free, essentially non-subliming dibasic acid mixture of succinic, glutaric and adipic acids having a boiling point of [about] 150-210°C, in a volatilizable flux vehicle, formed of a volatilizable organic solvent. The dibasic acid mixture is present in sufficiently dilute solution in the solvent (e.g., generally below about 10% concentration, preferable at most about 7.5% concentration), so as to be capable of essentially completely volatilizing during heat-soldering to leave the soldering site essentially completely free from ionic residue.

In particular, the rosin-free flux comprises a rosin-free solution of about 0.2-1% of the three-acid mixture and 99-99.8% of a volatilizable organic solvent as the flux vehicle, such as an aliphatic or cycloaliphatic alcohol, an aliphatic carboxylic acid ester, or mixture thereof.

The vehicle of the rosin-free flux may also optionally contain a slight diluent amount of de-ionized water. As used herein, a "slight" amount of water means at most about 1% of the total vehicle.

The organic solvent may be an alcohol such as a lower boiling or lower aliphatic alcohol, typically a lower alkyl alcohol or lower alkanol, such as ethyl, n-propyl, isopropyl, n-butyl, or sec-butyl, alcohol, or higher boiling aliphatic or cycloaliphatic alcohol, such as tetrahydrofurfuryl alcohol (about bp 178°C), and the like, or other such volatilizable aliphatic or cycloaliphatic alcohols in which the flux contents are soluble. As used herein, "lower" aliphatic, alkyl or alkanol means a chain of less than 5 carbon atoms. The alcohol is typically isopropyl alcohol (sp.g. 0.78).

The organic solvent may also be any other appropriate solvent such as an aliphatic carboxylic acid ester of lower boiling point, e.g., below about 200°C, or higher boiling point, e.g., below about 250°C. The aliphatic carboxylic acid ester is especially an aliphatic dicarboxylic acid dilower alkyl ester or ester mixture, typically an alkanedioic acid dilower alkyl ester (lower alkyl alkanedioate) or ester mixture, such as succinic, glutaric and adipic acid dimethyl ester, or a succinic, glutaric and adipic acid dilower alkyl ester mixture such as about 10-20% dilower alkyl succinate, 60-70% dilower alkyl glutarate and 10-20% dilower alkyl adipate, and, particularly, a mixture of refined methyl diesters of succinic, glutaric and adipic acids, or other such volatilizable ester in which the flux contents are soluble.

Such a preferred mixture of refined methyl diesters is sold under the trade designation "DBE" solvent (DuPont Co.), as a liquid of about average molecular weight (m. wt.) 159, 5.3% solubility in water (20°C), flash point 100°C, viscosity 2.4 cst. (25°C), and surface tension 35.6 dynes/cm (20°C), which has a boiling point of about bp 196-225°C and a specific gravity of 1.092 (20°C), and contains 99.5% total ester content (min.), comprising of about 16.5% dimethyl succinate, 66% dimethyl glutarate and 17% dimethyl adipate, plus approximately 0.2% methanol, 0.1% water (max.) and less than 10 ppm hydrogen cyanide.

Other such refined methyl diesters or diester mixtures are those sold under the following trade designations (DuPont Co.):

"DBE-2" solvent, as a liquid of about average molecular weight of 163, 4.2% solubility in water (20°C), flash point 104°C, and viscosity

2.5 cst. (25°C), which has a boiling point of about 210-225°C and a specific gravity of 1.081 (20°C), and contains 99.5% total ester content (min.), comprising of about 0.5% dimethyl succinate, 76% dimethyl glutarate and 23% dimethyl adipate, plus approximately <0.1% methanol and 0.1% water (max.).

"DBE-3" solvent, as a liquid of about average molecular weight of 173, 2.5% solubility in water (20°C), flash point 102°C, and viscosity 2.5 cst. (25°C), which has a boiling point of about 215-225°C and a specific gravity of 1.068 (20°C), and contains 99.5% total ester content (min.), comprising of about 0.5% dimethyl succinate, 10% dimethyl glutarate and 89% dimethyl adipate, plus approximately <0.1% methanol and 0.3% water (max.).

"DBE-4" solvent, as a liquid of about average molecular weight 146, 7.5% solubility in water (20°C), flash point 94°C, and viscosity 2.5 cst. (25°C), which has a boiling point of about 196°C and a specific gravity of 1.121 (20°C), and contains 99.5% total ester content (min.), comprising of about 99.5+ % dimethyl succinate, plus approximately <0.1% methanol and 0.1% water (max.).

"DBE-5" solvent, as a liquid of about average molecular weight 160, 4.3% solubility in water (20°C), flash point 107°C, and viscosity 2.5 cst. (25°C), which has a boiling point of about 210-215°C and a specific gravity of 1.091 (20°C), and contains 99.5% total ester content (min.), comprising of about 0.6% dimethyl succinate, 99% dimethyl glutarate and 0.1% dimethyl adipate, plus approximately 0.1% methanol and 0.1% water (max.).

"DBE-9" solvent, as a liquid of about average molecular weight 156, 5% solubility in water

(20°C), flash point 94°C, and viscosity 2.4 cst. (25°C), which has a boiling point of about 196-215°C and a specific gravity of 1.099 (20°C), and contains 98.5% total ester content (min.), comprising of about 25% dimethyl succinate, 73% dimethyl glutarate and 1.5% dimethyl adipate, plus approximately 0.3% methanol and 0.5% water (max.).

The aliphatic carboxylic acid ester, e.g., where it has a boiling point of from about 196°C to above about 200°C, is preferably used in admixture with an above type alcohol to lower the solvent boiling point.

Similarly, the solvent may be a cyclic ketone such as a cycloaliphatic, including azacycloaliphatic (i.e., N-heterocyclic), ketone, e.g., cyclopentanone, cyclohexanone, N-methyl-2-pyrrolidone (about bp 202°C), or other such volatilizable ketone in which the flux contents are soluble. The cyclic ketone may also be used in admixture with an above type alcohol and/or ester to lower the solvent boiling point.

Typically, the rosin-free flux of the present invention consists essentially of a solution of about 0.5-1% three-acid mixture and 99-99.5% lower aliphatic alcohol, or of about 0.2-1% three-acid mixture, 2-10% aliphatic dicarboxylic acid dilower alkyl ester, 88-97.6% lower aliphatic alcohol and 0.2-1% water. The percentages of three-acid mixture, alcohol, ester and water are based on the total solution. The alcohol and ester may be of the same above type used for the rosin flux, and are especially isopropyl alcohol and such aliphatic dicarboxylic acid dilower alkyl ester or ester mixture, such as succinic, glutaric and adipic acid dimethyl ester, or succinic, glutaric and adipic acid dilower alkyl ester mixture.

The ester is preferably a mixture of about 10-20% dilower alkyl succinate, 60-70% dilower alkyl glutarate and 10-20% dilower alkyl adipate, and, particularly, the refined methyl diesters of succinic, glutaric and adipic acids, sold under the trade designation "DBE" solvent (DuPont Co.), as noted above. The ester may also favourably be one of the type sold under the trade designations "DBE-2", "DBE-3", "DBE-4", "DBE-5" and/or "DBE-9" (DuPont Co.), as noted above.

The rosin-free flux can be used in soldering electronic circuit board components, and surprisingly has adequate fluxing action, despite the absence of rosin, due to the three-acid mixture makeup, whilst leaving minimal ionic residue after soldering.

The aliphatic carboxylic acid ester is not sufficiently acidic to act as a flux or to activate the three-acid mixture, but it has been found unexpectedly that the ester enhances the fluxing action of the three-acid mixture in the rosin-free flux due to its comparatively low surface tension (e.g., 35.6 dynes/cm). This enables it to serve as a strong wetting agent to aid spreading of the three-acid mixture on the parts to be joined, for improved soldering, whilst still leaving only a trace amount of ionic residue after soldering.

Where water is present, it serves to hydrolyze the ester and enhance its wetting action. However, ethylene glycol or a similar hydrolysis inhibiting agent may be included to control the extent of hydrolysis of the ester that occurs in the presence of water. This ester hydrolysis inhibiting agent may be present in an amount up to about an equivalent amount to that of the water present, and will thereby control the free acid content of the aqueous flux

solution.

Use of the ester advantageously decreases the amount of three-acid mixture required in the rosin-free flux.

5 The three-acid mixture is desirably present in the rosin-free flux in sufficiently dilute solution in the volatilizable solvent used to be capable of essentially completely volatilizing during heat-soldering to leave the soldering site essentially free
10 from ionic residue.

 Generally, if the amount of the three-acid mixture in the rosin-free flux is below about 0.2% of the flux, the fluxing action is insufficient for the heat-soldering operation. On the other hand, if the
15 three-acid mixture amount is above about 1%, more particularly, above about 2%, especially above about 5%, and generally above about 7.5%, or at least above about 10%, of the total flux, the tendency is concordantly progressively increased during heat-soldering for the ionic residue of the rosin-free flux
20 to exceed an acceptably low level.

 That acceptably low level is one that avoids the need for a washing step, as well as one which is attainable without the trouble and expense of
25 supplemental heating of the soldering site to raise the ambient temperature sufficiently above the soldering temperature for artificially or extraneously ensuring the essentially complete boiling-off of the flux constituents.

30 Therefore, it is recommended for practical, efficient soldering, when using the rosin-free flux in circuit board soldering applications, to provide the three-acid mixture in an amount preferably below about 5%, more preferably, below about 2%, and, to get the

best results, not greater than about 1%, of the total flux. This will leave an essentially ionic residue-free soldering site after the normally conducted heat-soldering operation, without splattering, subliming or local deposition of the flux constituents.

In the case of other soldering applications, where stronger fluxing action is necessary or desirable, and larger amounts of the three-acid mixture are employable to attain this action in using the rosin-free flux, the three-acid mixture amount may exceed about 1%, or about 2%, or even about 5%, of the total flux. In these circumstances, the amount of the three-acid mixture may even be increased up to about 7.5%, but will generally be less than about 10%, of the total flux.

Consequently, the actual amount of the three-acid mixture in the total rosin-free flux will be selected in dependence upon the nature of the metals being soldered, the degree of fluxing action required, and the soldering temperature contemplated for conjointly achieving effective fluxing action, molten solder flow and essentially complete volatilization of the flux constituents during the operation to leave an essentially non-corrosive and ionic residue-free soldered product.

In the rosin-free flux, the solvent is preferably miscible with water to enable water to be added optionally as a diluent to decrease solvent cost and enhance foamability of the flux, thereby aiding its spreading action. As the solvent and water boil off during soldering, their presence is not detrimental to the product. No more than a minor amount of water is used so as to inhibit splattering and deposition of residue at the soldering site, and possibly solder ball

formation, that adversely affect product quality. As an essentially ionic residue-free product is desired, de-ionized water is used to avoid increasing the ionic residue.

5 In heat-soldering metal surfaces, solder is applied to the surfaces in the presence of an effective amount of the flux in coating disposition on the surfaces, and at a temperature sufficient for molten flow of the solder and for volatilizing the flux to
10 leave the site essentially ionic residue-free. The soldering may be at conventional temperature, e.g., about 200-500°C, preferably about 250-350°C. For example, circuit board components may be soldered at the lower end of the temperature range and other
15 connections at the higher end of the range.

 The solder may be of any known type such as tin-lead solder, e.g., 60% Sn - 40% Pb of mp 191-193°C, or eutectic tin-lead solder, e.g., 63% Sn - 37% Pb of mp 183°C.

20 The flux is applied to the surfaces to be joined by conventional techniques, e.g., foaming, wave fluxing, spraying, brushing, rolling, and dipping, and the solder is applied to the flux-coated surfaces in usual manner, e.g., drop dispensing, or wave soldering,
25 to form the solder deposit. Then, the soldered surfaces are contacted with one another to join them at the soldering temperature, which also causes boiling-off of the flux constituents.

30 Normally, the attaining of a low ionic residue at the site is a function of the soldering temperature used during the operation. Thus, the three-acid mixture amount in the rosin-free flux is selected to achieve adequate fluxing action and essentially complete volatilization of the three-acid

mixture under the given soldering conditions so as to assure the attaining of such a low ionic residue.

5 Simple test runs may be used to optimize the three-acid mixture amount needed in the flux for the intended purposes at the given soldering temperature whilst also satisfying the aim of leaving a low ionic residue at the soldering site.

10 In sum, the invention provides a non-corrosive flux for soldering metals (e.g., tin plate, copper, brass, nickel, etc.), wherein the three-acid mixture imparts properties to the flux significantly different from those of the individual acids, for adequate fluxing action, yet leaving minimal ionic residue.

15 Particular advantages of the flux of the invention include:

(1) A three-acid mixture maximum boiling range, ~~[e.g.]~~ 150-210°C, that is significantly below the 235°C boiling point of succinic acid, its component of lowest boiling temperature.

20 (2) A three-acid mixture which does not sublime like its component succinic acid, and thus does not condense on adjacent areas, e.g., of circuit boards, during soldering, even though adequate precaution is not taken to minimize this effect.

25 (3) A composition of pleasant odour and that does not form noxious and pungent break-down products during soldering.

30 (4) A three-acid mixture that costs less than each of its constituents that could be used individually as an activator.

(5) A three-acid mixture usable as a rosin-free flux.

(6) The attaining of the above-listed

advantages with a three-acid mixture as essential component, whether in purified state or not, and thus contemplating commercial purity three-acid mixtures, whilst providing a stable flux of good cleaning action leaving so low a residue after soldering that no corrosive property is exhibited and no residue removal is needed.

The proportions of the three acids to each other in the three-acid mixture, and of all components in the flux, are selected to provide surface tension properties and a boiling point that enhance flux spreading and "wetting" of the surfaces being soldered and volatilization with innocuous decomposition without splattering, subliming or local re-deposition.

At most, only a trace amount of residue is left on the product. The ionic content of this residue, expressed as micrograms per square centimetre equivalent of NaCl (per Omega^(R.T.M.) Meter measurement, as later explained), is very low, i.e., below about $5 \mu\text{g}/\text{cm}^2$, and especially below about $1.2 \mu\text{g}/\text{cm}^2$ for the rosin-free flux.

As used herein, the term a "trace" amount means a very small amount that is less than about $5 \mu\text{g}/\text{cm}^2$, i.e., a microgram amount corresponding to less than five millionths of a gram (0.000,001 g) per sq. cm. area (cf. Hackh's Chemical Dictionary, 4th ed. 1969; p. 686: "trace" - a very small quantity, usually less than 5 gamma per gm; p. 288: "gamma" - 10^{-6} gm; p. 429: "microgram" - μg , gamma, one-millionth of a gram).

On using the flux of the invention, cleanliness tests for residual ionic contamination (per said Omega Meter measurement) showed that unwashed soldered electronic circuit boards had ionic residues below a trace amount, while corresponding soldered

boards after washing in Freon TMS (DuPont Co.), a chlorinated solvent, had only slightly lower residues. Thus, use of the flux of the invention affords a reliable quality product of acceptably low ionic residue without cleaning, and, even with cleaning, the ionic residue is only slightly further reduced.

The treatise, Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., John Wiley & Sons, provides a review of "Dicarboxylic Acids" (vol. 7: 614-625), i.e., the saturated, linear aliphatic series of dicarboxylic acids (diacids), from which melting and boiling point data as to the first nine of these organic dibasic acids are compiled in Table A.

TABLE A - Melting and Boiling Points

Total carbon atoms	UIPAC name	Common name	mp °C	bp °C
2	ethanedioic	oxalic	187 (dec)	
3	propanedioic	malonic	134-136 (dec)	
4	butanedioic	succinic	187.6-187.9	
5	pentanedioic	glutaric	98-99	200 2.7 kPa
6	hexanedioic	adipic	153.0-153.1	265 13.3 kPa
7	heptanedioic	pimelic	105.7-105.8	272 13.3 kPa
8	octanedioic	suberic	143.0-143.3	279 13.3 kPa
9	nonanedioic	azelaic	107-108	286.5 13.3 kPa
10	decanedioic	sebacic	134.0-134.4	294.5 13.3 kPa

*To convert kPa to mm Hg, multiply by 7.5:

2.7 kPa x 7.5 = 20 mm Hg; 13.3 kPa x 7.5 = 100 mm Hg.

From that same treatise, data as to the ionization constants of these diacids are also compiled in Table B.

TABLE B -- Ionization Constants in Water

<u>Diacid</u>	<u>Temp., °C</u>	<u>K1</u>	<u>K2</u>
oxalic	25	5.36×10^{-2}	5.42×10^{-5}
malonic	25	1.42×10^{-3}	2.01×10^{-6}
succinic	25	6.21×10^{-5}	2.31×10^{-6}
glutaric	25	4.58×10^{-5}	3.89×10^{-6}
adipic	25	3.85×10^{-5}	3.89×10^{-6}
pimelic	18	3.19×10^{-5}	3.74×10^{-6}
suberic	18	3.05×10^{-5}	3.85×10^{-6}
azelaic	18	2.88×10^{-5}	3.86×10^{-6}
sebacic	25	3.1×10^{-5}	3.6×10^{-6}

Selected characteristics based on Tables A and B, and the molecular weights of these diacids are given in Table C.

TABLE C - Selected Characteristics

Acid	Formula		M.Wt.	mp °C	bp °C	K ₁
oxalic	HOOC	- COOH	90	187d		5.36×10^{-2}
malonic	HOOC	CH ₂ COOH	104	135d		1.42×10^{-3}
succinic	HOOC(CH ₂) ₂	COOH	118	188	200*	6.21×10^{-5}
glutaric	HOOC(CH ₂) ₃	COOH	132	98.5	265**	4.58×10^{-5}
adipic	HOOC(CH ₂) ₄	COOH	146	153	272**	3.85×10^{-5}
pimelic	HOOC(CH ₂) ₅	COOH	160	106	279**	3.19×10^{-5}
suberic	HOOC(CH ₂) ₆	COOH	174	143	286.5**	3.05×10^{-5}
azelaic	HOOC(CH ₂) ₇	COOH	188	107.5	294.5**	2.88×10^{-5}
sebacic	HOOC(CH ₂) ₈	COOH	202	134		3.1×10^{-5}

* 20 mm Hg

**100 mm Hg

That treatise points out that these diacids are crystalline solids, whose melting points decrease as the aliphatic chain length (m. wt.) increases, with alternation of some physical properties of neighbouring members of the series such as oscillating melting point, water solubility and ease of decarboxylation or decomposition, but not of others such as boiling point, density and dielectric constant. Whereas the odd-numbered acids melt lower than their neighbours, e.g., the 5 carbon atom glutaric acid melting much lower than the neighbouring 4 carbon atom succinic acid and 6 carbon atom adipic acid, their boiling points increase with increasing molecular weight.

The boiling points of the lower (m. wt.) diacids are difficult to measure as they sublime, dehydrate or decompose, the even-numbered carbon atom acids being more resistant to decarboxylation or decomposition than the odd-numbered acids preceding them. Their thermal decomposition is sensitive to catalytic effects of impurities, environment and the decomposition products themselves, and results in decarboxylation to a monocarboxylic acid or anhydride formation, with water elimination, succinic and glutaric acids forming cyclic anhydrides and adipic acid forming a polymeric (linear) anhydride.

Malonic and glutaric acids are extremely water-soluble, the remaining even-numbered acids being only moderately soluble, solubility alternating between higher values for the odd-numbered acids and lower values for their even-numbered neighbours, yet rapidly decreasing with increasing chain length (m. wt.). Oxalic and malonic acids are strong acids and the higher homologues (m. wt.) are progressively weaker. Whilst the odd-numbered acids have lower

ionization constants than their even-numbered neighbours, the ionization constant values become almost constant for all the acids above adipic acid.

Elsewhere, that treatise notes that malonic acid loses carbon dioxide on heating above its melting point, and in aqueous solution, undergoes decarboxylation at 70°C (vol. 14: 794-795); that succinic acid sublimates when heated below its 188°C melting point, dehydrates at its melting point, and forms a cyclic anhydride, succinic anhydride having mp 119.6°C (vol. 21: 848-849); and that adipic acid, unlike glutaric acid and succinic acid, does not readily form a cyclic anhydride, but decomposes to cyclopentanone above 225°C (vol. 1: 510-513).

The Merck Index, 10th ed. 1983, Merck & Co., Rahway, N.J., shows similar data as to these nine diacids, especially their boiling points at normal pressure (760 mm Hg). It indicates that oxalic acid sublimates at 157°C, decomposes at higher temperature, and is hygroscopic and poisonous; that malonic acid melts with decomposition at about 135°C; that succinic acid has mp 185-187°C and bp 235°C with partial conversion to the anhydride (of mp 119.6°C and bp 261°C); that glutaric acid has mp 97.5-98°C and bp 302-304°C with very slight decomposition; that adipic acid has mp 152°C and bp 337.5°C, and is not hygroscopic; and that pimelic acid tends to sublime.

Oxalic and malonic acids are undesirable for this invention because of their low molecular weights, strong acidity and high dissociation constants, and the fact that oxalic acid sublimates at 157°C and is hygroscopic whilst malonic acid decomposes at its 135°C melting point, thereby adversely affecting the flux characteristics and causing large ionic residues, e.g.,

from decomposition and sublimation products.

Pimelic and higher acids are undesirable for this invention because of their cost, and high molecular weights and boiling points (which increase with their increasing molecular weights) that may adversely affect the characteristics and adequacy of boiling-off of the flux. Pimelic acid is not only costly, but also may splatter and sublime to expose the circuit board to local deposition of sublimation or decomposition constituents detracting from product quality.

Whilst succinic acid also tends to sublime, and glutaric acid is quite water-soluble, compared to non-hygroscopic adipic acid, on using these three acids as a mixture in the above-stated proportions, the average molecular weight and depressed boiling point of the mixture, as opposed to the individual acids, seem to impart efficient spreading action to the flux, and the higher content of the lower boiling point glutaric acid seems to aid boiling-off of the lower content higher boiling point succinic and adipic acids, as it has been found that the flux spreads without voids, does not splatter and leaves a low residue.

The three-acid mixture or TAM used for the rosin-free flux of the invention may be from any source, such as a commercial mixture of succinic, glutaric and adipic acids in which the three acids are in the desired proportions.

A first commercial mixture is a blend of the three acids available from DuPont Canada, Inc. (DuPont Canada), of good solubility, mild acidity (pH 2.95), melting range 90-130°C and boiling range 170-195°C, which has:

TAM Formulation No.1 - assay 97.0% (min.),

26-30% succinic acid, 55-59% glutaric acid and 11-15% adipic acid, plus 3% acid anhydrides (average), 0.8% succinimide (max.), 0.6% glutarimide (max.), 0.3% water (max.), 1 ppm copper (max.), 1 ppm vanadium (max.) and 5 ppm iron (max.). Typically, it has an assay of 97.6%, 27.7% succinic acid, 56.6% glutaric acid and 13.2% adipic acid, plus 2.7% acid anhydrides, 0.7% succinimide, 0.56% glutarimide, 0.08% water, 0.28 ppm copper, 0.1 ppm vanadium and 1.9 ppm iron; or it has about 27% succinic acid, 57.5% glutaric acid and 11.6% adipic acid, plus about 4% acid anhydrides, 0.7% succinimide, 0.5% glutarimide and 0.2% water.

A second commercial mixture is the product, designated "DBA", available from DuPont Co., Wilmington, DE (DuPont), of 20% water solubility (18°C/64°F), which has:

TAM Formulation No.2 - 18-28% succinic acid, 51-61% glutaric acid and 15-25% adipic acid, plus 1% organic nitrogen compounds, 0.2% nitric acid, 0.02% copper and 0.01% vanadium, and is available in a 50% concentration solution of the three acids in de-ionized water, sp.g. 1.106, having 26% succinic acid, 55% glutaric acid and 18% adipic acid, plus 0.3% nitric acid.

A third commercial mixture is a dicarboxylic acid product available from BASF Corp., Parsippany, NJ, of about 10% water solubility (room temp.), and about 100-130°C melting range and 150-210°C boiling range, which has:

TAM Formulation No.3 - assay of 97% (min.), 25-30% succinic acid, 42-47% glutaric acid and 25-30% adipic acid, plus 2.3% 2,5-pyrrolidinedione and 2,6-piperidinedione, and 0.5% water.

A fourth commercial mixture is the product,

designated "Diacides AGS", available from Rhone-Poulenc Inc., Princeton, NJ, of about 10% water solubility (room temp.) and 100-130°C melting range, which has:

TAM Formulation No.4 - 18-25% succinic acid, 50-55% glutaric acid and 20-25% adipic acid, plus 1.4% succinic anhydride, and particularly 19.5% succinic acid, 51.6% glutaric acid and 22.6% adipic acid, plus 1.4% acid anhydrides (as succinic anhydride), 0.06% nitrogen (kjeldahl), 0.3% water, 0.4 ppm copper, 0.06 ppm vanadium and 2.4 ppm iron.

These TAM formulations are especially usable as the three-acid mixture, with the components in the range of about 18-30% succinic acid, 51-61% glutaric acid and 11-30% adipic acid.

It was quite unexpected that these three-acid mixtures, per TAM formulations No.1-4, which are not especially purified, perform satisfactorily in the flux to provide consistent solderability under the relatively rigid conditions extant in electronic circuit board component soldering, yet leave the site essentially free from ionic residue and avoid a washing step, despite the impurities in such commercial grade mixtures.

This is especially so in view of the above indication in the Kirk-Othmer treatise that thermal decomposition of these diacids is sensitive to catalytic effects of impurities, and potentially those listed in commercial TAM formulations No.1-4.

The costs of chemicals in pure and commercial grade form are influenced by many factors, yet provide useful comparisons. Recently noted costs of the three pertinent acids in pure form, and the next higher acid, pimelic, are compared in Table D.

TABLE D - Comparative Costs of Individual Acids

<u>Acid</u>	<u>Unit Cost</u>	<u>Calculated Cost Per Kg</u>	
Succinic	\$126.90/2.5kg	\$ 50.76	50.76
Glutaric	14.20/25g	568.00	-
Adipic	24.60/2kg	12.60	12.60
Pimelic	61.25/100g	-	612.50
Total		631.36	675.86
Average		210.45	225.28

Arbitrarily taking equal amounts of the three acids as a mixture, the cost comes to an average cost of \$210.45/kg, and substituting pimelic for glutaric acid increases it to \$225.28/kg, and even higher if it is substituted for succinic or adipic acid. Any such substitution would change the properties of the resulting mixture, given the differences in melting and boiling points among these acids and the increase in average molecular weight imparted by the heavier pimelic acid component, aside from the objectionable tendency of pimelic acid to sublime.

More important, the cost of the commercial purity mixtures of succinic, glutaric and adipic acids, per TAM formulations No.1-4 above, is roughly \$1.25/kg (\$0.57/lb), which is far less than the above calculated average cost of a mixture of the pure acids, and a comparable mixture in which pimelic acid is substituted for glutaric acid would be even more expensive. Despite the lower purity of these commercial mixtures in the flux and the need to limit the ionic residue to, at most, a trace amount, they surprisingly perform eminently satisfactorily for the purposes of the invention, without having to formulate the mixture from the high purity individual acids at

high cost.

Based on the above Merck Index data, their melting and boiling points may be taken generally as set forth in Table E.

TABLE E - Approximate Melting and Boiling Points

	<u>Acid</u>	<u>mp °C</u>	<u>bp °C</u>
10	Succinic	186	235
	Glutaric	98	303
	Adipic	<u>152</u>	<u>337.5</u>
	Total	436	875.5
	Average	145°C	292°C

15 The commercial mixtures of these acids have 90-130 and 100-130°C mp ranges, and 170-195 and 150-210°C bp ranges, of average mp 110°C and bp 180°C well below the Table E averages. The commercial
20 mixture mp range is below the boiling points of succinic and adipic acid, and its bp range is below the boiling point of succinic acid, i.e., the lowest of the three acids.

25 A distinct benefit of the commercial mixture depressed boiling range is that the acids boil away to leave a low ionic residue, so that the impurities in the commercial grade mixtures and high acidity of their dibasic acid content have been found not to be a problem. When the three acids are in the above-noted
30 ranges, optimum results are achievable for adequately coating the surfaces to be soldered, whilst inhibiting splattering, sublimation and local re-deposition.

Despite the high acid content and impurities in the commercial mixtures, the constituents boil off

at ambient soldering conditions, avoiding a large ionic residue and a washing step for its removal, and the low ionic residue that is left occurs without supplemental heating as normally used to prevent local re-deposition of constituents. The flux assures more consistent solderability in attaining a low ionic residue product, and soldering occurs without causing annoying or noxious odours on the circuit boards or fixtures, and provides a circuit board product whose surfaces have a desired post-solder dryness and non-tack condition without use of special steps.

As to the rosin-free flux of the invention, the inclusion of the aliphatic carboxylic acid ester, especially said "DBE" solvent (DuPont Co.), with the lower aliphatic alcohol, such as isopropyl alcohol (IPA), is particularly desirable because of the low surface tension imparted to the three-acid mixture solution formulation, as when used for foam, spray and wave application. The replacement of a rosin component by the ester component correspondingly lowers the rosin-free flux cost, and use of the ester component permits convenient adjustment of the amount of the three-acid mixture component by replacement of a portion of this component by the ester component at comparable cost.

The rosin-free flux of the invention is of especial advantage in achieving an extremely low ionic content flux residue on soldering, at a relatively low materials cost. Most significant is the fact that the rosin-free flux can provide a soldered product in usable form as produced, without the trouble and expense of a washing step to remove ionic residue and/or of supplying supplemental heat during the soldering to assist volatilization of the flux constituents.

Typically, the rosin-free fluxes are useful in electronic circuit board soldering, to attain in all cases a significant decrease in the number of product rejects from shorts, voids and like defects, without a washing step.

Employing a combination of the alcohol component and the ester component as organic solvent in the rosin-free flux to form the desired sufficiently dilute solution of the three-acid mixture for achieving an essentially ionic residue-free soldering site is particularly preferred. The alcohol (e.g., IPA) is a very low-cost polar liquid component of relatively low boiling point and acceptably low surface tension below that of water (the surface tension of water being about 72.8 dynes/cm, at 20°C). The ester (e.g., DBE) is a liquid component of low cost comparable to that of the three-acid mixture, and of suitably low boiling point and especially low surface tension.

These conjoint beneficial features are attained in the rosin-free flux, such as where the alcohol and ester are in the relative proportion to each other of about 1-99% alcohol and 99-1% ester, especially 50-99% alcohol and 50-1% ester, and the three-acid mixture is in a concentration therein of

less than 10%, especially not more than about 7.5%. Stated another way, the alcohol and ester components are advantageously in the ratio of about 1-99 parts alcohol to 99-1 parts ester, and especially 50-99 parts alcohol to 50-1 parts ester, and their combined total represents more than 90% of the rosin-free flux solution, the corresponding less than 10% remainder of the solution being the three-acid mixture.

As inclusion of the ester component advantageously lowers the corresponding amount of the three-acid mixture needed in the rosin-free flux, the amount of the ester component will usually be sufficient where the alcohol component and ester component are in the proportion of about 50-99% alcohol and 50-1% ester, for a three-acid mixture dilute solution concentration therein of about 0.2-7.5%, especially 0.2-5%, and particularly 0.2-2%.

As the optional inclusion of de-ionized water further lowers the cost and aids foaming where desired, its hydrolyzing effect on the ester component can be readily controlled by conjoint inclusion of a hydrolysis inhibiting agent. The influence of the low surface tension property of the ester component on the alcohol component and included water will thereby be retained, whilst any increase in acidity of the three-acid mixture-containing solution, traceable to ester hydrolysis, will be minimized.

The present application has been divided out from GB-A-9106903.9, which discloses low-residue organic soldering fluxes containing both a dibasic acid mixture and a rosin. The following examples 1 to 4, in which all parts and

percentages are by weight unless otherwise indicated, are set forth by way of illustration and not limitation of the invention claimed.

5 EXAMPLE 1 - Low TAM Rosin-Free and Water-Free
 Alcoholic Flux

 (a) TAM Formulation No.3 (BASF) is used
 directly with IPA to form a low TAM content rosin-free
 and water-free flux for spray application, (i) by
10 dissolving 5 g TAM in 995 g IPA to form an isopropyl
 alcohol solution of about 0.5% TAM content, and (ii) by
 dissolving 10 g TAM in 990 g IPA to form an isopropyl
 alcohol solution of about 1% TAM content.

 (b) The procedure of (a) is repeated using
15 instead TAM Formulation No.4 (Rhone-Poulenc).

 (c) The procedure of (a) is repeated using
 instead TAM Formulation No.1 (DuPont).

 Each of the fluxes of EXAMPLE 1 is usable
 according to EXAMPLE 11 of GB-A-9106903.9, like the
20 flux of EXAMPLE 10 of GB-A-9106903.9, by spray
 application to the circuit board for attaining similar
 results, the TAM in this case serving as flux
 sufficient to clean the surfaces being soldered due to
 the highly acidic nature of the three acids present,
25 yet of sufficiently dilute concentration to avoid undue
 corrosive action whilst leaving a low ionic residue.

EXAMPLE 2 - Low TAM Rosin-Free Aqueous Alcoholic
 Flux

30 7 ml of the above-noted "DBE" solvent (DuPont
 Co.) liquid (DBE) of bp 196-225°C and sp.g. 1.092
 (20°C), containing 99.5% total ester content (min.), of
 about 16.5% dimethyl succinate, 66% dimethyl glutarate
 and 17% dimethyl adipate, plus about 0.2% methanol,

0.1% water (max.) and less than 10 ppm hydrogen cyanide, totalling 7.644 g (1.092×7) DBE, were combined with 3 ml or 2.9388 g (3×0.9796) TAM solution [Formulation No.3 (BASF)] of 0.8445 g (3×0.2815) TAM (28.7%), 1.1292 g (3×0.3764) IPA (38.4%) and 0.9651 g (3×0.3217) water (32.9%), plus 340 ml or 265.2 g (0.78×340) IPA, to form 350 ml or 0.09 U.S. gal. of flux.

The flux, by calculation, contained 0.8445 g TAM (0.3%), 7.6440 g DBE (2.8%), 266.3292 g ($265.2 + 1.1292$) IPA (96.6%) and 0.9651 g water (0.3%), total 275.7828 g of sp.g. 0.7880 ($275.7828/350$), for a TAM content of 0.3% corresponding to 0.2 vol.% ($0.8445/350$).

EXAMPLE 3 - Low TAM Rosin-Free Aqueous Alcoholic Flux

The procedure of EXAMPLE 2 was repeated, this time using 125 ml or 136.5 g (1.092×125) DBE with 50 ml or 48.980 g (50×0.9796) TAM solution, of 14.075 g (50×0.2815) TAM (28.7%), 18.820 g (50×0.3764) IPA (38.4%) and 16.085 g (50×0.3217) water (32.9%), plus 3610 ml or 2815.8 g (0.78×3610) IPA, to form 3785 ml or 1 U.S. gal. of flux.

The flux, by calculation, contained 14.075 g TAM (0.5%), 136.5 g DBE (4.6%), 2834.62 g ($2815.8 + 18.82$) IPA (94.4%) and 16.085 g water (0.5%), total 3001.28 g of sp.g. 0.7929 ($3001.28/3785$), for a TAM content of 0.5% corresponding to 0.4 vol.% ($14.075/3785$).

At 100 pts TAM, the EXAMPLE 2 flux had about 905 pts DBE, 31537 pts IPA and 114 pts water, and the EXAMPLE 3 flux had about 970 pts DBE, 20139 pts IPA and 114 pts water.

Rosin-free low TAM-content fluxes of EXAMPLES 2-3 were used in wave-soldering electronic circuit board components as in EXAMPLE 11 of GB-A-9106903.9.

When subjected to the above (a) Omega Meter tests of EXAMPLE 11 of GB-A-9106903.9, without washing to remove ionic residue and before applying the conformal-coating, a circuit board (board 23) soldered using the EXAMPLE 2 rosin-free flux had an ionic residue of $1.0128 \mu\text{g}/\text{cm}^2$, as NaCl equivalent, whilst one (board 24) soldered using the EXAMPLE 3 rosin-free flux had an ionic residue of $1.1597 \mu\text{g}/\text{cm}^2$, as NaCl equivalent, both of which are surprisingly below $1.2 \mu\text{g}/\text{cm}^2$, and well below the rosin flux (a) test ionic residues of the washed boards 6-8 of Table L of EXAMPLE 11 of GB-A-9106903.9.

When thereafter subjected to the above (b) ion chromatograph tests of EXAMPLE 11 of GB-A-9106903.9, the board (board 23) soldered using the EXAMPLE 2 rosin-free flux had a total extracted anionics residue of $6.1559 \mu\text{g}/\text{cm}^2$, whilst that (board 24) soldered using the EXAMPLE 3 rosin-free flux had a total extracted anionics residue of $12.2705 \mu\text{g}/\text{cm}^2$, both of which are also surprisingly well below the rosin flux (b) test total extracted anionics residues of all the boards 1-22 of Table L of EXAMPLE 11 of GB-A-9106903.9.

Boards 23-24, like boards 1-22 of Table L of EXAMPLE 11 of GB-A-9106903.9, were of the same size, each having a total area of 230 cm^2 (total of both sides of the board).

These markedly improved low ionic (and extracted anionic) residue results for the rosin-free flux of the invention (boards 23-24), compared to those for the rosin flux (boards 1-8) of GB-A-9106903.9, and more pointedly compared to those for the known rosin fluxes No.2 and No.3 (boards 9-22 of GB-A-9106903.9), are consistent with the above explanation that the (a) test of EXAMPLE 11 of GB-A-9106903.9 detected increase in ionic residue of the Freon TMS (R.T.M.) washed boards soldered with known fluxes No.2 and No.3 (boards 11-12 of GB-A-9106903.9), compared to the levels of the unwashed boards soldered with known flux No.2 (boards 9-10 of GB-A-9106903.9), and that this is traceable to a residual amount of rosin that serves as an acidic constituent-retaining matrix.

This is emphasized by the analogous results per the (b) tests of EXAMPLE 11 of GB-A-9106903.9 as to total extracted anions, since the rosin-free flux lacks such a potential acidic constituent-retaining matrix and its (b) test residue levels are far below the concordant total extracted anionic levels for all the rosin fluxes of Table L of EXAMPLE 11 of GB-A-9106903.9.

Because of its lack of any rosin, the rosin-free flux is particularly suitable, not only to avoid problems associated with the ionic constituent-retaining matrix functioning of rosin, but also to avoid problems associated with circuit board soldering in those instances when the presence of even a slight residue of rosin could cause difficulties in achieving efficient electrical contact between certain mechanical switch contact surfaces, as earlier explained.

Accordingly, it can be appreciated that the specific embodiments described are merely illustrative of the general principles of the invention.

Claims:

1. A low-residue organic soldering flux consisting of a rosin-free, essentially non-subliming dibasic acid mixture of succinic, glutaric and adipic acids having a melting point of 90-130°C and a boiling point of 150-210°C in a dilute solution in a volatilizable organic solvent, said mixture being capable of essentially completely volatilizing during use as a flux on a soldering site during heat-soldering of said soldering site, so as to leave the soldering site essentially free from any ionic residue from the flux.
2. A low-residue organic soldering flux according to claim 1, in which the dibasic acid mixture contains by weight 15-30% succinic acid, 40-63% glutaric acid and 10-30% adipic acid.
3. A low-residue organic soldering flux according to claim 1, in which the solvent is selected from an aliphatic or cycloaliphatic alcohol, an aliphatic carboxylic acid ester, or mixtures thereof.
4. A low-residue organic soldering flux according to claim 1, in which the flux contains a slight diluent amount of de-ionized water.
5. A low-residue organic soldering flux according to claim 1, in which the dibasic acid mixture is present in an amount of less than 10% by weight of the flux.
6. A low-residue organic soldering flux comprising a rosin-free solution of, by weight, 0.2-1% of an essentially non-subliming dibasic acid mixture containing 15-30% succinic acid, 40-63% glutaric acid and 10-30% adipic acid, and 99-99.8% of a volatilizable solvent selected from an aliphatic or cycloaliphatic alcohol, an aliphatic carboxylic acid ester, or mixtures thereof.



7. A low-residue organic soldering flux according to claim 6, in which the flux contains a slight diluent amount of de-ionized water.

5 8. A low-residue organic soldering flux according to claim 6, in which the flux consists essentially of 0.5-1% dibasic acid mixture and 99-99.5% of a lower aliphatic alcohol.

10 9. A low-residue organic soldering flux according to claim 8, in which the alcohol is isopropyl alcohol.

10 10. A low-residue organic soldering flux according to claim 6, in which the flux consists essentially of 0.2-1% of the dibasic acid mixture, 2-10% of an aliphatic dicarboxylic acid dilower alkyl ester, 88-97.6% of a lower aliphatic alcohol and 0.2-1% of de-ionized water.

20 11. A low-residue organic soldering flux according to claim 10, in which the ester is a mixture of by weight 10-20% dilower alkyl succinate, 60-70% dilower alkyl glutarate and 10-20% dilower alkyl adipate.

25 12. A low-residue organic soldering flux according to claim 10, in which the ester is a mixture of by weight 16.5% dimethyl succinate, 66% dimethyl glutarate and 17% dimethyl adipate, having a boiling point of 196-225°C, and the alcohol is isopropyl alcohol.

30 13. A method of heat-soldering metal surfaces which comprises applying a solder to the metal surfaces in the presence of an effective amount of a low-residue organic flux according to claim 1 in coating disposition on the metal surfaces, and at a temperature sufficient for molten flow of the solder and for volatilization of the flux from the metal surfaces, so



as to leave the surfaces essentially free from ionic residue from the flux.

14. A method of heat-soldering metal surfaces according to claim 13, in which the soldering is effected at a temperature of 200-500°C.

15. A method of heat-soldering metal surfaces according to claim 13, in which the soldering is effected with a tin-lead solder.

16. A method of heat-soldering metal surfaces which comprises applying a solder to the metal surfaces in the presence of an effective amount of a low-residue organic flux according to claim 6 in coating disposition on the metal surfaces, and at a temperature sufficient for molten flow of the solder and for volatilization of the flux from the metal surfaces, so as to leave the surfaces essentially free from ionic residue from the flux.

17. A method of heat-soldering metal surfaces which comprises applying a solder to the metal surfaces in the presence of an effective amount of a low-residue organic flux according to claim 12 in coating disposition on the metal surfaces, and at a temperature sufficient for molten flow of the solder and for volatilization of the flux from the metal surfaces, so as to leave an ionic residue of at most about $1.2 \mu\text{g}/\text{cm}^2$ equivalent of sodium chloride on said surfaces.

18. A soldered product produced by a method according to claim 17.

19. A low-residue, rosin-free, water-free alcoholic flux substantially as hereinbefore particularly described in any one of Examples 1 to 3 of the accompanying specification.