



(51) International Patent Classification:

C09D 193/04 (2006.01) *C09D 191/00* (2006.01)
C08L 93/04 (2006.01) *C08L 91/00* (2006.01)
H05K 3/28 (2006.01) *B23K 35/36* (2006.01)

(21) International Application Number:

PCT/US2014/011740

(22) International Filing Date:

15 January 2014 (15.01.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13/831,452 14 March 2013 (14.03.2013) US

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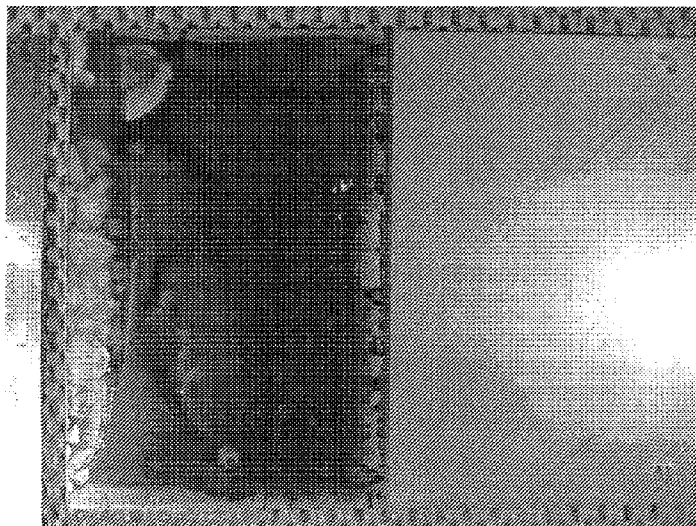
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

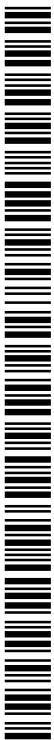
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(54) Title: GUM ROSIN PROTECTIVE COATING AND METHODS OF USE

FIG. 6



(57) Abstract: A rosin composition includes a gum rosin, an emulsifier, and a randomizing additive. The rosin composition may be applied to circuit cards for protection of the circuit card during storage. The rosin composition is solderable and is also easily removed for the soldering of components.



TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG). **Published:**

— with international search report (Art. 21(3))

GUM ROSIN PROTECTIVE COATING AND METHODS OF USE

TECHNICAL FIELD

[0001] The invention is directed to gum rosin compositions and protective coatings including the compositions.

BACKGROUND

[0002] The shelf life of a circuit card (cc) assembly prior to manufacturing is about 6 months in normal processing environments. Considering that the world's electronic suppliers have expanded globally to include locations such as China and India, it is likely that a printed wiring board (PWB) may sit in transit for up to 4 months prior to reaching the circuit assembly manufacturer. Since environmental restrictions regarding use of hazardous materials have been implemented in the U.S. and Europe, lead-based paints and lead-based surface finishing of electronic devices have been replaced with lead-free versions. However, lead-free surface finishes contain high levels of tin which form tin whisker protrusions in the presence of corrosion or high levels of oxidation. These metal protrusions can transmit high levels of electrical current when bridging to adjacent circuit traces.

[0003] Printed wiring board (PWB) surface finishes require a well-defined environment and/or a long shelf life to allow for reliable solder joints. The surface finish degradation due to airborne contaminants and oxide surface formation are both significant factors in determining PWB soldering shelf life. Electroless nickel over immersion gold (ENIG) has been used in the past for military application. Commercially robust surface finishes such as immersion tin, immersion silver, Organic Solderability Preservative (OSP), and other imidazole coatings are used to form a barrier and extend the shelf life on the surface finishes to be soldered. The degree to which the soldering process is impeded depends on the degradation thickness and surface area of the OSP and the imidazole coatings. As time passes, a "worse than" condition can occur using these standard organic coatings. For OSP-coated PWBs, the plastic can be contaminated with finger oils and other manufacturing support materials that deteriorate the solderability of the coating. For non-coated PWBs, the oxide which forms on the metallized surface raises the melting point of the solder when reflow occurs. If high enough concentrations of oxide permeate the unprotected PWB, a cold solder joint will be formed and will fail prematurely. This becomes critical for fine pitch, high density components in electronic designs.

1 [0004] Accordingly, a protective coating to preserve the solderability of a circuit card during storage is desired to improve the manufacturing of circuit card assemblies and printed wiring boards.

5 SUMMARY

[0005] In some embodiments of the present invention, a rosin composition includes a gum rosin, an emulsifier, and a randomizing additive. The gum rosin may be water white gum rosin. The emulsifier may be either solvent-based or semi-aqueous, and may include polyvinyl alcohol. The randomizing additive may be selected from hydrocarbon oils, naturally occurring oils, glycols, and combinations thereof.

10 [0006] In some embodiments of the present invention, a method of protecting a circuit card for storage is provided, where the method includes applying a rosin composition including a gum rosin, an emulsifier, and a randomizing additive, drying the circuit card to obtain a coated circuit card, storing the circuit card, and optionally removing the rosin composition from the coated circuit card. The removal of the rosin composition may include using a soapy solution and/or an organic solvent.

15 BRIEF DESCRIPTION OF THE DRAWINGS

[0007] These and other features and advantages of the present invention will be better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings, wherein:

20 [0008] FIG. 1 is a photograph of a copper test board prior to cleaning, according to embodiments of the present invention;

[0009] FIG. 2 is a photograph of a cleaned, rinsed, and dried copper test board;

[0010] FIG. 3 is a photograph of one of two thumb prints being placed on the left side of the demarcated, clean, copper test board;

25 [0011] FIG. 4 is a photograph of one of two thumb prints being placed on the right side of demarcated, clean, copper test board;

[0012] FIG. 5 is a photograph of the copper test board of FIG. 4, after a gum composition has been applied to one side of the demarcated copper test board, according to embodiments of the present invention;

30 [0013] FIG. 6 is a photograph of the copper test board of FIG. 5, after a gum composition has been applied to one side and the copper test board has aged for 8 months at room temperature with 30 to 50% humidity, according to embodiments of the present invention;

1 [0014] FIG. 7 is a photograph of a cleaned copper test board of FIG. 6, after a gum composition has been applied to the left side, and the copper test board has aged for 8 months at room temperature with 30 to 50% humidity, according to embodiments of the present invention;

5 [0015] FIG. 8 is a photograph of the solderable copper test board of FIG. 7, after 8 months of aging, according to embodiments of the present invention.

DETAILED DESCRIPTION

10 [0016] In some embodiments of the present invention, a gum rosin composition is a protective coating that is effectively and easily removed. A gum rosin composition according to embodiments of the present invention includes a gum rosin, an emulsifier, and a randomizing additive. In some embodiments, the gum rosin composition has the properties
15 of being able to coat and protect a copper test board or any part of a circuit card such that solderability is preserved during storage and/or transport. That is, the gum rosin composition not only protects, but is solderable, thereby eliminating the need to remove the coating. Additionally, the gum rosin composition disclosed herein may be removed from the board without loss of solderability. In some embodiments, a gum rosin composition of the present
20 invention is used as a protective coating for a circuit card assembly (CCA) that preserves solderability of the circuit card.

[0017] In some embodiments, examples of gum rosins include, but are not limited to, gum rosins having the following grades: N, X, XX, W-G, and W-W. Gum rosins are
25 available from a variety of companies, including but not limited to Alfa Aesar, Ward Hill, MA, USA; Arizona Chemical Company, Pensacola, FL, USA; Mead Westvaco, Richmond, VA, USA; GEA Barr-Rosin, Maidenhead Berkshire, UK; Cray Valley HSC, Paris La Defense Cedex, France; Jai Bharat Resin and Chemical, Rishikesh, India; Balram Sri Krishna Overseas, Amritsar (Punjab), India; Shanghai Xiaoxiang Chemical Company, Shanghai,
30 China; Shanghai Polymer Commodities, Ltd., Shanghai, China; Dalian Chemical Import and Export Group Company, Dalian City (Liaoning Prov.), China; Fuzhou Farwell Import and Export Company, Fuzhou, China; Guangxi Qinzhou Capital Success Chemical Company, Qinzhou City, China; and Roveda Ind. Quim Ltda, Santa Catarina, Brazil.

35 In some embodiments, the gum rosin is water white gum rosin. An emulsifier of embodiments of the present invention includes solvent-based emulsifiers or semi-aqueous emulsifiers. Examples of solvent-based emulsifiers include, but are not limited to,

1 trichloroethane, acetone isopropyl alcohol (IPA), an IPA and water combination, toluene,
benzene, 2-propanol (IPA), methyl ethyl ketone (MEK), toluene/acetone/methyl ethyl ketone
(MEK) and IPA combination, 1,1-dichloroethane, isoamyl acetate, cellusolve acetate,
5 acetone, xylene, 1,1,1,1-tetrachloromethane, 1,1,2,2-tetrachloroethene, 1,1,1-trichloroethane,
1,1,2-trichloroethane, 1,1-dichloroethane, 1,1-dichloroethene, 1,2-dichloroethane, 1,2,-
dichloroethene, 1,1-dichloro-1-bromoethane, 1,1-dichloro-1-bromoethene, 1-bromo-1chloro-
2-chloroethene, 1,1,1-tribromoethane, 1,1,2-tribromoethene, and combinations thereof.

[0018] Examples of semi-aqueous emulsifiers include, but are not limited to, ethylene
10 glycol in water, diethylene glycol in water, polyethylene glycol (PEG) in water, polyethylene
di-glycol in water, terpene-based organic compounds in water, organic sulfate compounds in
water, and combinations thereof. Non-limiting examples of organic sulfate compounds
include dimethyl sulfoxide, diethyl sulfoxide, sodium methylsulfinylmethide,
15 trimethylsulfonium iodide, dimethylsulfoniopropionate, and methylsulfonylmethane in an
emulsion of isopropyl alcohol and water.

[0019] In some embodiments, a semi-aqueous emulsifier includes polyethylene glycol
(PEG) with the caveat that if the carbon chain is buttressed where the addition group is
20 attached (multifunctional glycols), then solvency of the higher molecular weight constituents
do not form emulsions. In some embodiments, a semi-aqueous emulsifier includes PEG
having a molecular weight of about 5,000 daltons or less. In some embodiments, a semi-
aqueous emulsifier includes PEG having a molecular weight of about 3,000 daltons or less.
In some embodiments, a semi-aqueous emulsifier includes PEG having a molecular weight of
25 2,000 daltons or less. In some embodiments, a semi-aqueous emulsifier is an adipate
derivative of PEG.

[0020] Examples of polyethylene diglycols for use as a semi-aqueous emulsifier include,
but are not limited to, methyl diglycol, ethyl diglycol, diethylene glycol dibutyl ether, butyl
30 diglycol, glycol butyl ether, allyl diglycol, and combinations thereof.

[0021] Terpene chemistry is known to work as a semi-aqueous cleaning solvent based on
methyl buta-1, 3 diene (hemiterpene C_5H_8). A terpene compound in solutions of warm water
will dissolve the polymerization product of water immiscible fluxes at concentrations as low
as 5 percent. Additionally, monoterpenes ($C_{10}H_{16}$); sesquiterpenes ($C_{15}H_{24}$); diterpenes
35 ($C_{20}H_{32}$); sesterpenes ($C_{25}H_{40}$); and triterpenes ($C_{30}H_{48}$) in solution will dissolve the
polymerization product of water immiscible fluxes.

1 [0022] Phosphate substitutions of the isoprene will also work to dissolve the polymerization product of water immiscible fluxes. A non-limiting example of a terpene phosphate is isopentenyl pyrophosphate ($C_5H_{12}O_7P_2$)

5 [0023] Commercially available products of terpene (isoprene)-based cleaning solutions include: Bioact EC7R, Bioact EC7M, Axarel 36, Pinsol, Citraflor EG3, Citraflor EGS, Citraflor EGX, d-limonene FG, and d-limonene HG.

10 [0024] In some embodiments, a randomizing additive includes, but is not limited to, hydrocarbon oils, naturally occurring oils, and glycols. Examples of hydrocarbon oils include, but are not limited to, castor bean oil, corn oil, grape seed oil, olive oil, peanut oil, soybean oil, sunflower seed oil, walnut oil, avocado oil, flax seed oil, and combinations thereof. Examples of naturally occurring oils, include, but are not limited to, glycerin, hemp oil, jojoba oil, lanolin, tea tree oil, and wheat germ oil. Examples of glycols include, but are not limited to, polyethylene glycols (PEG), ethylene adipates, benzo-alkyl diols, and combinations thereof.

15 [0025] In some embodiments, a single randomizing additive may be used with the gum rosin and emulsifier. In other embodiments, however, combinations of at least two additives may be used. For example, a combination of two or more additives from the same group may be used, such as two or more hydrocarbon oils. Alternatively, in some embodiments, two or more additives from different groups may be used, such as one hydrocarbon oil and one naturally occurring oil, or one oil and one glycerol. Also, when the combination of additives includes two materials from the same group (e.g., two hydrocarbon oils), any mixing ratio may be used. Similarly, when the combination of additives includes at least two materials from different groups, any mixing ratio may be used. However, in some embodiments, when the combination includes a mixture of oils (either hydrocarbon or naturally occurring) and glycerols, the weight ratio of oil to glycerol ranges from about 5 to about 20% glycerol in oil. Longer chain oils (i.e., those having higher molecular weight) are less effective at randomizing the terpene polymer, while branched chain hydrocarbons are less effective than linear hydrocarbons. Ratios of glycerol to oil resulting in greater than about 20% glycerol in the oil, negatively affect the performance of the gum rosin composition compared to using the hydrocarbon oil by itself. In some embodiments, the mixtures of these randomizing additives are effective from about 3% to about 45% when mixed with solubilized gum rosin (i.e., gum rosin mixed with an emulsifier). Compatibilities of the randomizing additives vary in their long-term effectiveness. However, in general, for any combination or permutation of

1 the above, the higher the concentration of the randomizing agents the longer the curing time
for the protective coating.

5 **[0026]** Furthermore, the more emulsifier added to the protective base coat, the thinner the
protective coating in the dried coating. In some embodiments, the amount of emulsifier in
the gum rosin and emulsifier mixture is not more than about 30% by weight.

10 **[0027]** In some embodiments, a method of preparing a gum rosin coating composition
includes solubilizing a gum rosin at room temperature. For example, a gum rosin is added to
an emulsifier to form a solubilized gum rosin composition. The gum rosin and emulsifier are
15 mixed in a ratio of about 4 to about 8 parts gum rosin in combination with about 1 to about 3
parts emulsifier. In some embodiments, the gum rosin and emulsifier are mixed in a ratio of
about 8 parts gum rosin to about 2 parts emulsifier. The solubilized gum rosin composition is
then combined with a randomizing additive. After addition of the randomizing additive, the
20 solubilized gum rosin and randomizing additive composition is heated in a range from about
30 to about 90° C, and/or exposed to electromagnetic power sources. Exposure to
electromagnetic power forms a quasi-prepolymer gum rosin coating composition. A quasi
prepolymer is a mixture of a partially reacted polymer with excess resin which is combined
with an active curing agent or curative rich prepolymer. The net result is a polymer structure
that increases in molecular weight forming either a glue or a plastic.

25 **[0028]** In some embodiments, an optional surface stabilizer is added to the quasi-
prepolymer gum rosin composition. A surface stabilizer may decrease the tackiness of the
gum rosin composition. Examples of a surface stabilizer include, but are not limited to fluoro
surfactants such as Dupont's Zonyl 8857A and fluoro surfactants such as Omnova PolyFox
PF-651.

30 **[0029]** In some embodiments, the gum rosin composition according to embodiments of
the present invention includes a gum rosin, an emulsifier, a randomizing additive, as well as a
filler. A filler may be added to increase the viscosity of the composition and make the
composition more thixotropic. The filler may be a material that is either reactive or non-
35 reactive to the polymer chemistry. Non-limiting examples of a reactive material filler include
the addition of boric acid or succinic acid to the polyvinyl alcohol. Non-limiting examples of
a non-reactive material filler include fumed silica (CAB-O-SIL[®]), cut glass fiber, aluminum
oxide, fine powdered ceramics, non-conductive carbon nanotubes (CNT), carbon geodesic
balls (Buckyballs or fullerenes), natural organic based fine nut shell particles (particles of nut
shells), synthetic organic fine particles (finely ground nylon 66 or derivative), finely ground

1 glass beads (silica dioxide), and inorganic non-reactive fine powders (potassium sulphate). In
some embodiments, the filler used in the gum rosin coating composition is thermally stable
up to about 240 °C.

5 **[0030]** In some embodiments, a gum rosin coating composition of the present invention
may be applied as a protective coating. For example, a gum rosin coating composition of the
present invention may be applied to a printed wiring board (PWB) prior to assembly of a
circuit card assembly (CCA). An example copper test board is shown prior to cleaning in
FIG. 1, and after cleaning and drying in FIG. 2. FIGs. 3 and 4 show a copper test board being
10 marked with thumb prints for comparison of the solderability of the board, and FIG. 5 shows
the copper test board after application of the coating onto the surface of the left side (e.g., by
brushing). The coated surface is cured (i.e., allowed to dry) at room temperature or with
heating up to about 60 °C for about 2 hours. In some embodiments, partially assembled
15 PWBs are coated with the gum rosin composition of the present invention to protect both
components and boards in mid-process applications.

[0031] A PWB coated with a gum rosin composition as disclosed herein, may be placed
in storage. This coated PWB may be in storage, for example, for up to approximately one
year. FIG. 6 shows the copper test board of FIG. 5 after 8 months at room temperature at 30-
20 50% humidity.

[0032] In some embodiments, after removal from storage, the protective coating is
removed from the PWB. According to embodiments of the present invention, a protective
coating that has been applied to a surface may be solvated by immersion in a soapy water
25 solution. In some embodiments, the soapy water solution includes an industrial detergent.
Examples of an industrial detergent include Kyzen detergents, for example, Kyzen 4615
(Aquanox®, Kyzen Corp., Nashville, Tennessee). In some embodiments, the disclosed
protective coating is removed in a soapy water solution of 12% Kyzen 4615. In some
30 embodiments, the removal using a soapy water solution also includes heating up to about 65
to 70 °C. FIGs. 7 and 8 show the copper test board of FIG. 6 after cleaning with Kyzen 4615.
The left side of FIG. 7 which is shown in a closer view in FIG. 8, shows that the left side
which had the protective coating is solderable.

[0033] Alternatively, for water-sensitive device applications that have been assembled,
35 the protective coating may be solvated from a surface using solvents such as trichloroethane,
acetone, toluene, benzene, 2-propanol (IPA), and tetrachlorofluoroethane (i.e., freon). After

1 removal of the protective coating, the PWB is rinsed with de-ionized water, and then a flux is applied as necessary for the soldering of components.

5 [0034] In other embodiments, the gum rosin protective coating composition is adjusted such that the disclosed gum rosin flux/emulsifier/randomizing agent mixture is in a range from about 20 to about 100% by weight with the remaining components including an aqueous solvent or organic polymer solvent. An acrylic or modified acrylate-urethane coating has demonstrated good protective oxygen barrier performance. However, using such materials as polystyrene or other carbonyl modified polymer materials can be added in lower concentrations to the gum rosin flux composition in order for the protective coating to remain "cleanable" (i.e., removable).

10 [0035] In other embodiments of the present invention, the gum rosin protective coating composition as disclosed herein is applied and not removed before soldering. That is, the gum rosin protective coating composition as disclosed is capable of being soldered, thereby eliminating the step of removing the protective coating.

15 [0036] The following Example is presented for illustrative purposes only, and does not limit the scope or content of the present application.

20 [0037] Example

Isopropyl alcohol (emulsifier) was mixed with water white gum rosin at a ratio of 2 parts IPA to 8 parts water white gum rosin. This rosin and IPA mixture was stirred and heated at 23 °C to 30 °C for 2 hours. 1 part grape seed oil was added to 9 parts IPA gum rosin mixture to form a coat protective mixture. The coat protective mixture was coated onto a copper test substrate and allow to air dry overnight (FIG. 5). The copper test board was stored for 8 months at 30-50% humidity at room temperature. Following 8 months of storage, the protective coating was removed from the coated side of the copper test board with a soapy water solution of 12% Kyzen 4615 (Kyzen Corp., Nashville, Tenn.) heated to 65 ° C and the coating was brushed off into the cleaning solution. The copper test board was then rinsed with de-ionized water. Components can now be soldered to this board.

30 [0038] As disclosed herein, and for example, as shown in FIGs. 7-8, a water white gum rosin composition according to embodiments of the present invention, is an effective coating that can be removed leaving a solderable surface. This protective coating can act as an oxygen and moisture barrier to protect bare copper, solder or other shelf-life sensitive

1 material on the surface of, for example a PWB. As disclosed and shown herein, (e.g. FIG. 6),
the protective coating remains on the surface of the PWB after fabrication, and can remain on
the surface, for example, through shipment and in storage at the CCA manufacturer's site
until assembly is required. When necessary (e.g., for the soldering of components), the
5 protective coating on the surface of the PWB is easily removed by an aqueous or organic
solvent. The cleaned surface is highly active with low amounts of oxygen content or other
contaminants. This protective coating composition provides for a much higher first pass
yield and lower field unit failure in the manufacturing of CCAs.

10 **[0039]** While the present invention has been illustrated and described with reference to
certain exemplary embodiments, those of ordinary skill in the art will understand that various
modifications and changes may be made to the described embodiments without departing
from the spirit and scope of the present invention, as defined in the following claims.

1 WHAT IS CLAIMED IS:

1. A rosin composition, comprising:
a gum rosin;
an emulsifier; and
5 a randomizing additive.
2. The rosin composition of claim 1, wherein the gum rosin is a water white gum rosin.
3. The rosin composition of claim 1, wherein the emulsifier is selected from the group consisting of trichloroethane, acetone isopropyl alcohol (IPA), an IPA and water combination, toluene, benzene, 2-propanol (IPA), methyl ethyl ketone (MEK),
10 toluene/acetone/methyl ethyl ketone (MEK) and IPA combination, 1,1-dichloroethane, isoamyl acetate, cellusolve acetate, acetone, xylene, 1,1,1,1-tetrachloromethane, 1,1,2,2-tetrachloroethene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethane, 1,1-dichloroethene, 1,2-dichloroethane, 1,2,-dichloroethene, 1,1-dichloro-1-bromoethane, 1,1-dichloro-1-bromoethene, 1-bromo-1 chloro-2-chloroethene, 1,1,1-tribromoethane, 1,1,2-tribromoethene, and combinations thereof.
4. The rosin composition of claim 1, wherein the emulsifier is selected from the group consisting of ethylene glycols in water, diethylene glycols in water, polyethylene glycols (PEG) in water, polyethylene diglycols, terpene-based organic compounds, organic sulfate compounds in water, and combinations thereof.
5. The rosin composition of claim 4, wherein the PEG in water has a molecular weight of about 5,000 daltons or less.
6. The rosin composition of claim 4, wherein the polyethylene diglycols are selected from the group consisting of methyl diglycol, ethyl diglycol, diethylene glycol dibutyl ether, butyl diglycol, glycol butyl ether, allyl diglycol, and combinations thereof.
7. The rosin composition of claim 4, wherein the terpene-based organic compounds is selected from the group consisting of hermiterpenes, monoterpenes,

1 sesquiterpenes, diterpenes, sesterpenes, triterpenes, and phosphate-substituted isoprenes, and
combinations thereof.

5 8. The rosin composition of claim 1, wherein the randomizing additive is
selected from the group consisting of hydrocarbon oils, naturally occurring oils, glycerols,
and combinations thereof.

10 9. The rosin composition of claim 1, wherein the randomizing additive is
selected from the group consisting of castor bean oil, corn oil, grape seed oil, olive oil, peanut
oil, soybean oil, sunflower seed oil, walnut oil, glycerin, hemp oil, jojoba, lanolin, tea tree oil,
wheat germ oil, polyethylene glycol, ethylene adipate, and benzo-alkyl diol.

15 10. The rosin composition of claim 1, wherein the gum rosin and the emulsifier
are mixed in a ratio of about 4 to about 8 parts gum rosin to about 1 to about 3 parts
emulsifier.

20 11. The rosin composition of claim 1, wherein the randomizing additive is present
in an amount ranging from about 3 to about 45% by weight.

25 12. The rosin composition of claim 1, wherein the randomizing additive is present
in an amount of about 10% by weight.

13. The rosin composition of claim 1, further comprising a filler.

30 14. The rosin composition of claim 1, wherein the filler is selected from the group
consisting of hydrated sodium borate, boric acid, succinic acid, fumed silica, cut glass fiber,
aluminum oxide, fine powdered ceramics, non-conductive carbon nanotubes (CNT), carbon
geodesic balls, nut shell particles, ground nylon 66, a derivative of nylon 66, ground silica
dioxide, potassium sulphate, and mixtures thereof.

35 15. A method of protecting a circuit card for storage, the method comprising:
applying the rosin composition according to claim 1 on the circuit
card;

1

drying the circuit card to obtain a coated circuit card; and
removing the rosin composition from the coated circuit card.

5

16. The method of claim 15, wherein the removing of the rosin composition
comprises using a soap solution or an organic solvent.

10

17. The method of claim 16, wherein the removing of the rosin composition
comprises using an organic solvent selected from the group consisting of trichloroethane,
acetone, toluene, benzene, isopropyl alcohol, tetrachlorofluoroethane, and combinations
thereof.

15

18. The method of claim 16, wherein the removing of the gum rosin composition
comprises using a detergent.

20

19. A method of protecting a circuit card for storage, the method comprising:
applying the rosin composition according to claim 1 on the circuit
card;
drying the circuit card to obtain a coated circuit card; and
soldering the coated circuit card.

25

20. The method of claim 19, further comprising storing the coated circuit card for
up to one year.

30

35

FIG. 1

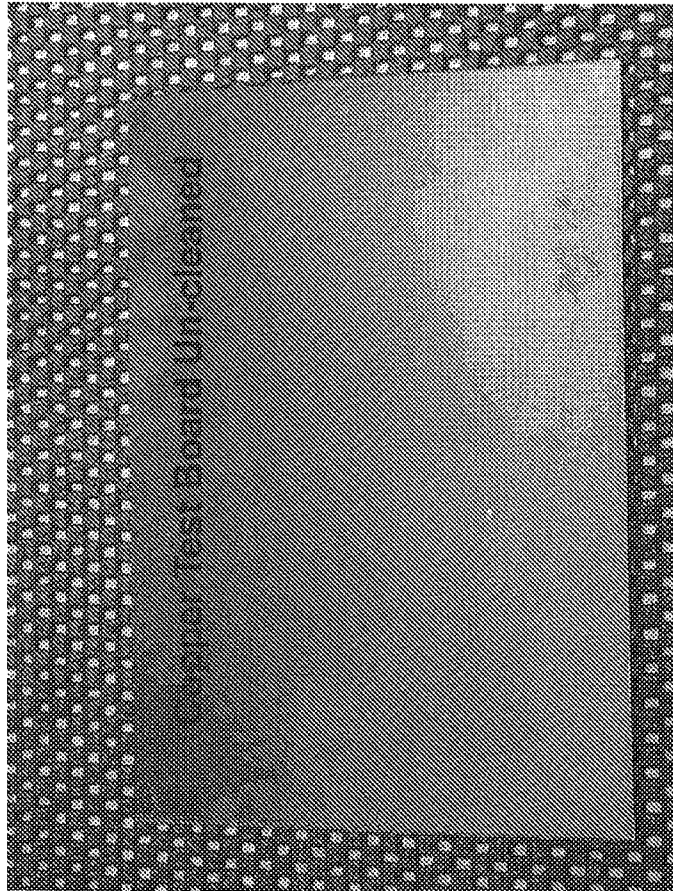


FIG. 2

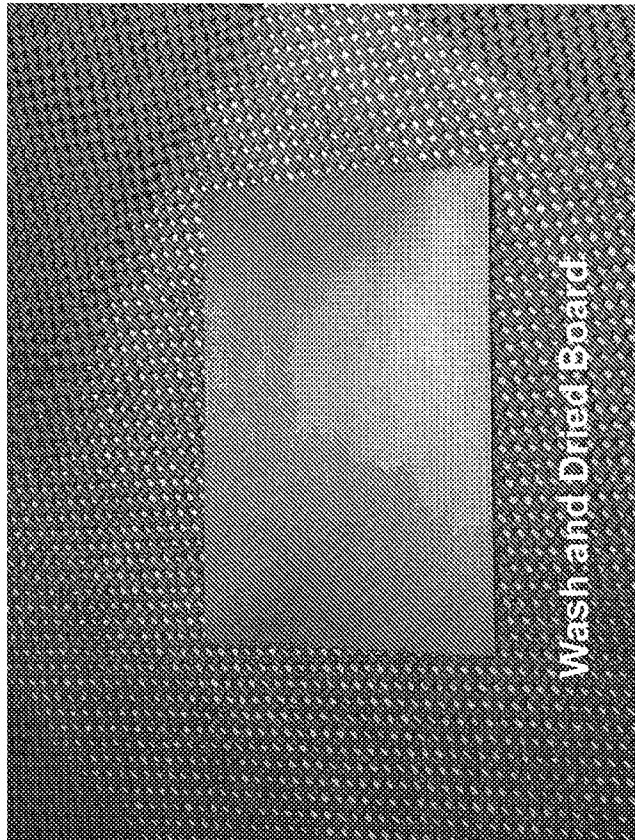


FIG. 3

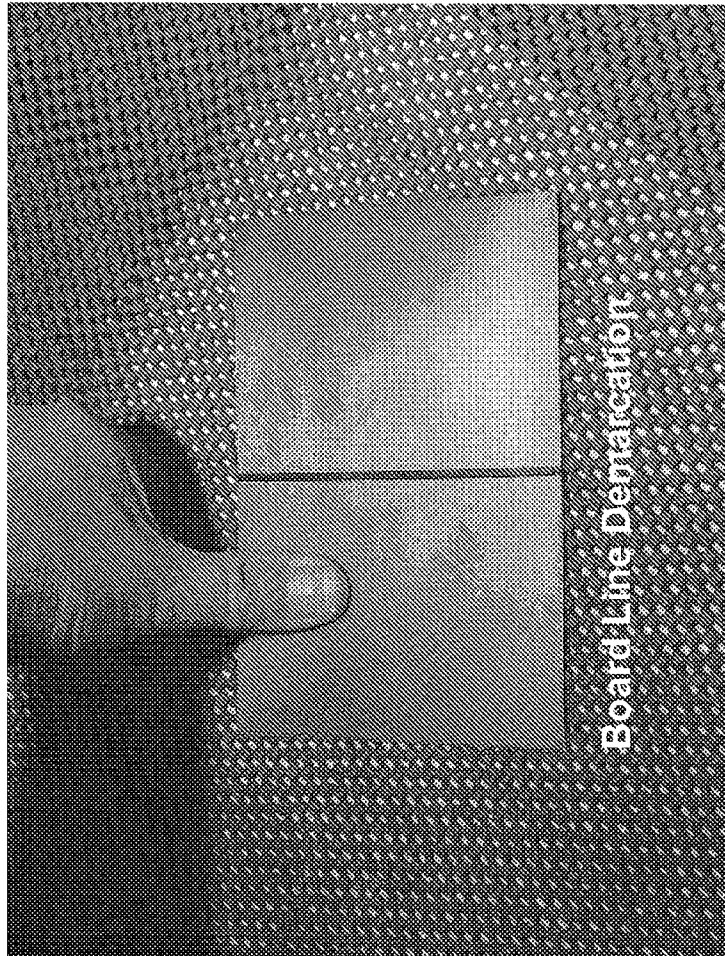


FIG. 4

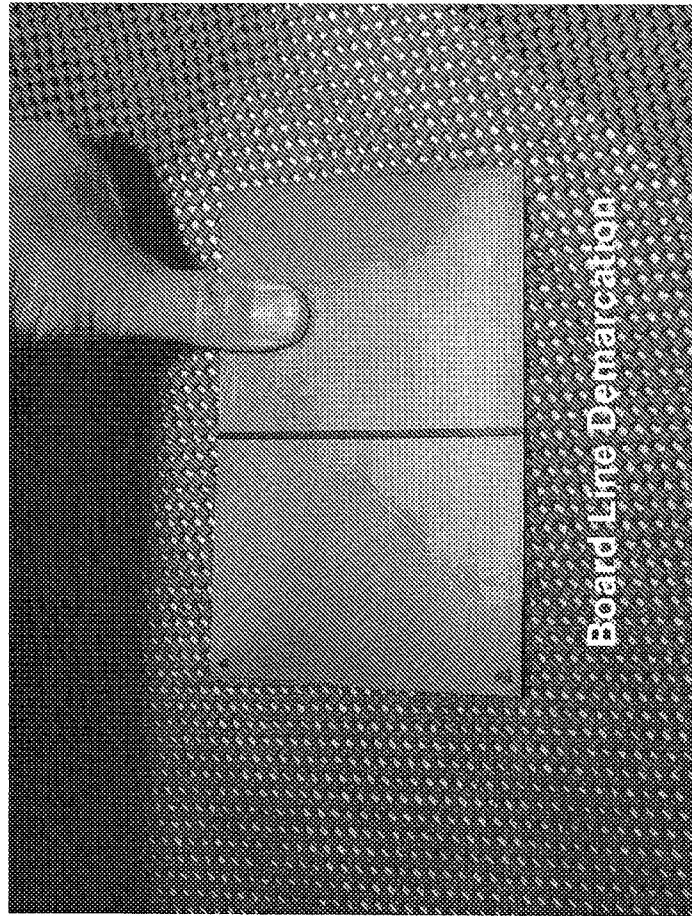


FIG. 5

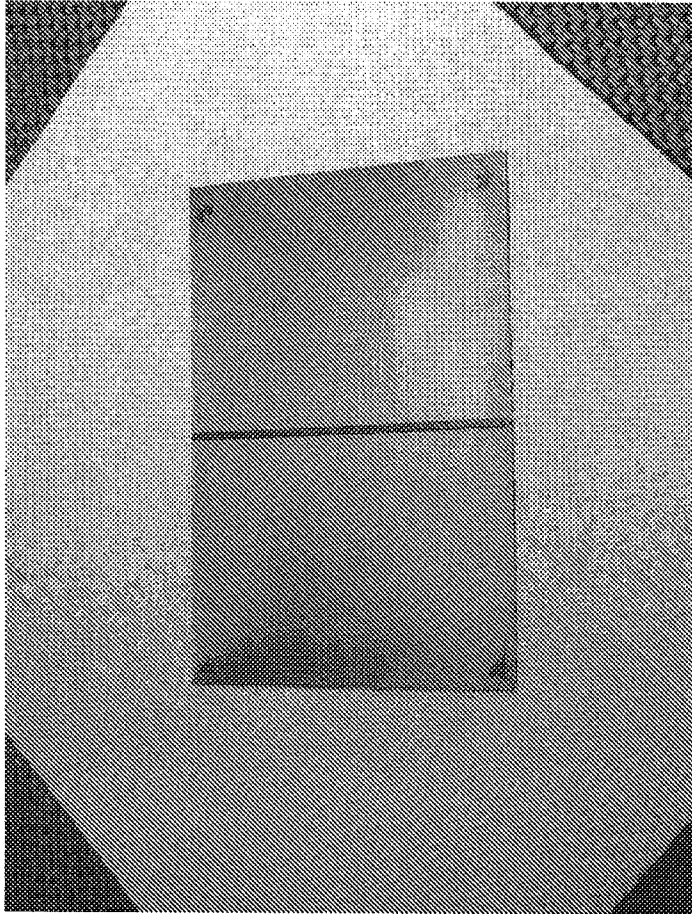


FIG. 6

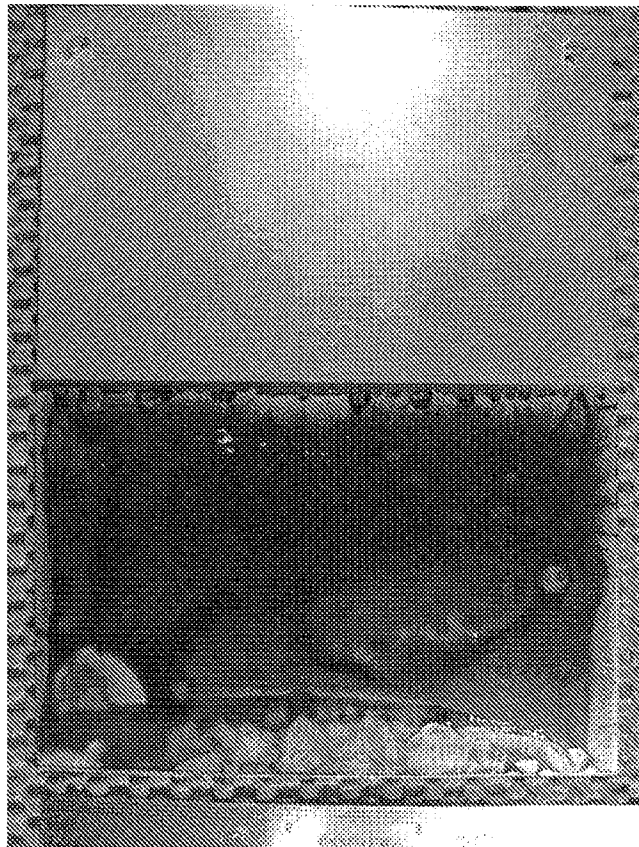
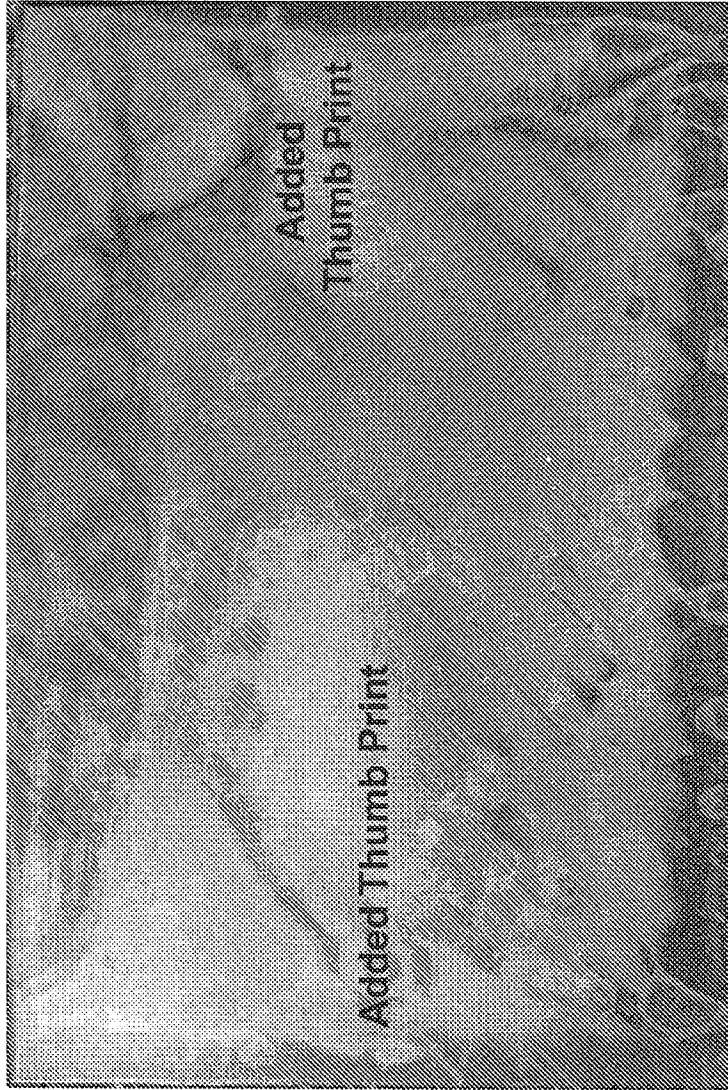


FIG. 7



FIG. 8



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/011740

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C09D193/04 C08L93/04 H05K3/28 C09D191/00 C08L91/00
 B23K35/36
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C09D C08L B23K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	EP 2 090 622 A2 (COLAS SA [FR]) 19 August 2009 (2009-08-19) paragraphs [0007] - [0033]; claims 1-6 -----	1-14
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search 3 April 2014	Date of mailing of the international search report 10/04/2014
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Gerber, Myriam
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/011740

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	US 3 708 448 A (IPPOLITO A ET AL) 2 January 1973 (1973-01-02) column 1, lines 12-24, 29-43; examples 1-8 -----	1-20
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