kester
CONNECTING INNOVATION™

THE NATURE OF WHITE RESIDUE ON PRINTED CIRCUIT ASSEMBLIES

by:
Dennis F. Bernier
Vice President, Research & Development
Kester

15 April 1988

Abstract

White residue remaining after cleaning circuit board assemblies can be caused by a variety of chemicals and reactions. Rosin and water-soluble fluxes, circuit board resins and epoxies, component materials and other contamination all contribute to this complex chemistry. This paper discusses many of the sources of the residues that seem to be an ever-increasing occurrence.

What is this white residue on the printed circuit assemblies? Why is the white residue suddenly appearing when it never happened before? What is causing the white residue? Why is this only and intermittent problem?

These are questions accompanying soldered circuit board assemblies sent to the Kester laboratory for analysis and, hopefully, some answers. The residue remains after cleaning the assembly to remove soldering flux.

The problem is not limited only to rosin fluxes and solvent cleaning, but also occurs when water soluble fluxes are used and when either flux type is removed with water. The soldering and cleaning processes involve so many chemicals in the flux, circuit board, components and cleaning agents that a complete understanding of the reactions is very difficult if not impossible.

There are white residue problems with water soluble fluxes and many of the causes not related to the flux compositions are the same as for rosin fluxes. The organic water soluble flux itself is more likely to oxidize and decompose than a rosin flux because generally the water soluble organic acids are not as heat stable as rosin acids. Halide (chloride and bromide) salts help reduce oxidation and improve activity but may result in metal salt residue that is not water soluble. Other decomposition products caused by the heat of soldering may also no be removed with water.

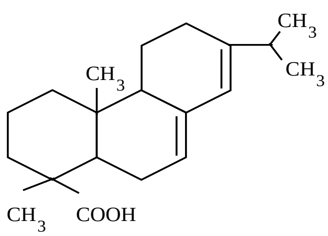
Rosin Flux more often has been used for electronic assemblies when the white residue problem arises. If rosin fluxes appear to be such a problem, why continue to use them? The answer is simple. Rosin fluxes are active enough to solder electronic assemblies and the residue has a very good insulation resistance. Typically rosin fluxes, including most activated types, have insulation resistances in the 10^{10} ohms or higher. The problem arises when it is required to remove the residue either because the assembly will operate hot (above 65°C) where the rosin becomes tacky, or the rosin might flake off and get between electrical contacts or just for aesthetics (not a good reason for cleaning).

Rosin is derived from pine trees. Gum rosin essentially is pine tree sap that has had approximately 20% turpentine distilled off. What remains is gum rosin. Wood rosin is obtained by boiling aged tree stumps. Tall oil rosin is a byproduct of the paper pulping process. Wood and tall ail rosin are similar to gum rosin but contain a different mixture of resin acids. The primary monobasic resin acids for the three main sources of rosin are typically distributed in the following percentages: -

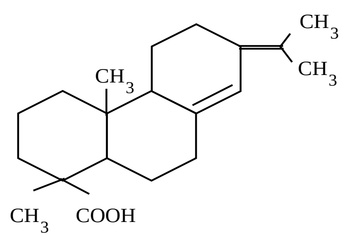
Acid	Gum	Wood	Tall Oil
Abietic	20	50	35
Neoabietic	16	5	5
Dehydroabietic	7	10	30
Palustric	30	10	10
Pimaric	5	5	5
Isopimaric	22	20	15

Generally, it is not good to have more than 30% of a particular acid as crystallization in solution may occur. Tall oil rosin also may contain an appreciable amount of fatty acids.

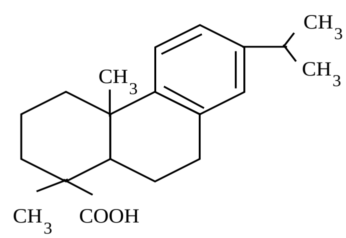
Because of the varying mix of resin acids, the chemistry can be very complex often times unpredictable. Rosin also may come from a variety of sources, including America, Portugal, China and Brazil. All vary in composition.



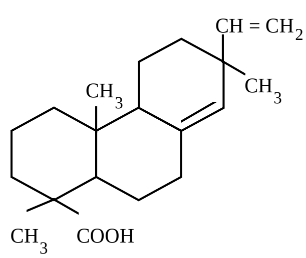
ABIETIC ACID



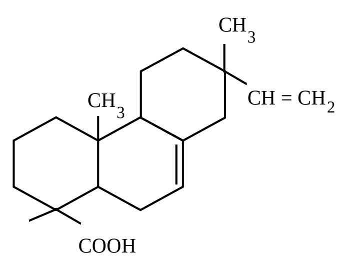
NEOABIETIC ACID



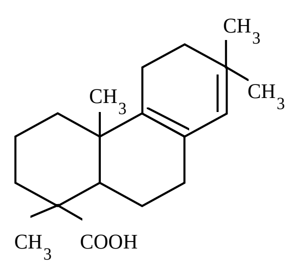
DEHYDROABIETIC ACID



PIMARIC ACID



ISOPIMARIC ACID



PALUSTRIC ACID

Though these six resin acids represent the major portion of the acids, there are a half dozen other isomeric forms included in smaller amounts. Rosin contains only abut 90% resin acids. To add to the chemical complexity, the other 10% is nonacidic materials. These neutral ingredients, more than 100 compounds, include: -

- resin acid esters
- fatty acid esters
- diterpene aldehydes and alcohols
- C_{19} - C_{31} hydrocarbons
- wax

So, when rosin is used as a flux, what can happen during the heat of soldering when the rosin is exposed to air and oxidized metal surfaces?

<u>Oxidation</u> of the rosin during heating involves the double bonds of the resin acids. The conjugated double bonds of the abietic type acids are particularly susceptible to oxidation by atmospheric oxygen because of the unsaturation. The reaction is one of oxidation, resulting in peroxides, hydroxy and keto compounds. The oxidized rosin is considerably less soluble in solvents than the original rosin and after cleaning a circuit board assembly, remains irregularly distributed over the surface as a white film. The most common type of circuit board on which this residue appears is the thick multilayer with ground planes . The excessive amount of heat required (heat is temperature for a time) results in oxidation of the rosin.

The overheating, usually exceeding 150°C, often has been said to cause polymerization of the rosin. There possibly is some formation of epoxide but polymerization is not likely to occur to any measurable extent at the soldering temperature (250°C) and without the presence of a catalyst.

This oxidation can be minimized by hydrogenating the resin acids to reduce the unsaturation. However, the soldering ability of the rosin is considerable reduce. This oxidized rosin appears to be the most common "white residue" appearing on soldered circuit boards. Chlorinated of fluorinated solvent, alcohols and saponifier/water cleaning seem to have little effect for removing this residue.

An industry "magic" method for removing this white residue, when it appears, has traditionally been to run the circuit board assembly across only the fluxer and preheater and remove it prior to soldering. Then when the assembly was cleaned in the normal manner, the white residue often would disappear. There is really nothing magic about the success of their process. If this white residue is oxidized rosin, melted resin acids should be a good reactive solvent to help remove the residue. In the laboratory evaluation, if the residue appear to be a film, sometime removable by wiping with a cloth, e have also used other acidic solutions to remove it. An alcohol-based organic acid flux is very effective in solubilizing the white reside. Also, other mild acidic solutions such as solder brightener have worked. A thirty second dip in these solutions followed by a 50:50 alcohol:water rinse usually removes the residue. This points directly at the rosin as the source. However, infrared, ultraviolet and HPLC analysis of the various lots of rosin show no chemical difference between a flux that leave white residue and one that does not.

<u>The acid carboxyl group</u> also reacts during soldering. Because tin can also be detected in the white residue, a portion (less than 10% by observation) of the reside may be a reaction product between tin oxide and the resin acids. The result is often referred to as tin abietate instead of tin resinate which is more correct since the resultant compound is formed also with the pimaric acids. The salts of pimaric and dehydroabietic acids are very insoluble in water or alcohol while those of abietic neoabietic and isopimaric acids are more soluble.

This reaction with metal oxides or hydroxides is slow because of molecular structure hindrance of the resin coaboxylic acid group. However, reaction does occur and residue results: -

$$2\ R\text{-}C00H + Cu0 \longrightarrow (R\text{-}C00)_2\ Cu + H_2\ 0$$

The copper salt is green and the tin salt is tan. Both appear not as crystalline salt but rather as a soapy film. This residue is usually mixed with the bulk of the rosin and is removed with rosin. However, when mixed with excessively oxidized rosin, the metal resinates also remain.

<u>Esterification</u> of the resin carboxyl group also is difficult because of steric hindrance, but at soldering temperature (250°C) the presence of glycol can result in resinate formation. Rosin esters are used in lacquers for wood finishing, adhesive and even chewing gum. The diverse selection of chemicals added to rosin fluxes can result in a number of residues which may be difficult to remove.

<u>Activators</u> which consist of halides (chlorides or bormides) and halogens capable of liberating halides also can result in whit residues. Listed here are a few of the commonly formed metal salts which may appear after soldering:-

Compound	Water Solubility (g/100cc)	Color
$CuC1_2$	70.6	green
CuC1	0.006	green
$CuBr_2$	very soluble	black
CuBr	very slightly soluble	white
$SnCl_2$	83.9	white
$SnBr_2$	85.2	pale yellow
$PbCl_2$	1.0	white
$PbBr_2$	0.8	white
$PbCO_3$	insoluble	white
$CuCO_3 \bullet Cu\ (OH)_2$	insoluble	green
Copper Resinate	insoluble	green
Tin Resinate	insoluble	tan

The halide activator improves the ability of the flux to remove metal oxides and also improve the heat stability of the rosin. However, the tradeoff is the type of residue that can result. Type R (plain rosin) and type RMA (small amount of halide) fluxes are more susceptible to oxidation. Type RA (0.1 0 0.5% halide) are more heat stable but can leave halide salts. Rosin with its high insulation resistance keeps the halides dormant but if the rosin is remove, leaving some halide salt behind, corrosion is possible.

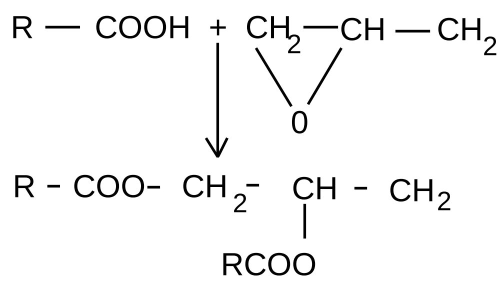
$$\begin{array}{c} Pb + 2HCl + Pb\,CO_3 \\ \downarrow \qquad \uparrow \quad CO_2 \text{ in air} \\ PbCl_2 + H_2O \end{array}$$

Lead chloride can form as an insoluble white residue on the solder surface. In the presence of moisture and carbon dioxide in the air, lead carbonate can form The liberated hydrochloric acid continues the corrosion cycle until a large growth of lead carbonate has occurred. This is more common with water soluble fluxes containing chloride but has been known to occur with highly activated rosin fluxes which have been incompletely removed. Typically if the white residue is on the solder, if a piece of wetted silver chromate test paper is placed on the residue for a minute, chloride or bromide can be detected by a change in the color of the paper from tan to white (chloride) or yellow (bromide). Most commonly copper salt is green and the white reside turns out to be lead chloride/carbonate salts. The lead chloride is not soluble enough to be removed with water and appears as a film on the solder.

<u>Solvent</u> (chlorinated or fluorinated) can be a source of chloride residue. Inhibitors are added to help prevent degradation or "souring", but in the presence of chlorides from flux and water from condensation the solvent can "go acid" and cause chloride formation.

<u>Solder mask</u> is also a major cause of white reside. Incompletely cured solder mask can be the result of formulation error, lack of heat for infrared cured type or ultraviolet cured type. Most solder mask related whit reside seems to be with the UV curable type, possibly because that is more prevalent or there really are control problems in applying it. Improper cure can be for simple reasons, the greatest being associated with the UV lamps. We have seen 15-20% difference in intensity from lamp to lamp. reflectors get dirty, and lamps wear out or get out of focus. The coating thickness also affects the cure. Soft solder mask can result in attack by the flux or cleaning chemicals. The best cure for UV solder mask seems also to include a thermal cycle. If the soldering process provides this heat to set up the mask, rosin or solder (as small spheres) can get stuck in the mask epoxy. Contamination under the solder mask can cause mealing or blistering of the mask, sometimes appearing to be residue. Over cured solder mask can crack, and if the mask was over solder plating, small solder spheres can extrude out to the surface. Solder mask usually is colored probably to see if it is there and to cover any blemishes on the circuit board. We have seen examples where the color has washed out of the mask, resulting in what looks like white residue.

<u>Laminate</u> also might be incompletely cured either because the board manufacturer made a mistake or the resin was misformulated. A typical thermosetting epoxy resin (FR-4) is based on the reaction between epichlorohydrin and tetrabromobisphenol A. The bromine is added for fire retardance. It is possible without complete cure of the epoxy for the carboxylic acid in the rosin to react with both the epoxy group and a hydroxyl group to form esters. Another possibility for white residue.



The brominated dihydric phenol thermally degrades at only 135°C. Without complete thermoset cure and with the rapid heating of soldering, it is possible for the hydrochloric acid in the flux (even type RMA) to attack, liberate the bromide and form lead bromide on the solder surface. This is another insoluble white residue.

Gray residue can wash up out of plated through holes to appear on the top of circuit board. This material may be organic additive in the solder plating in the holes or on the component leads. Another possibility is etching chemicals left in the holes.

Protective coatings on copper surfaces vary considerably in composition and, unfortunately, everybody assumes that this coating is compatible with the flux and cleaning agents. With increasing interest in solder mask over bare copper (SMOBC) if the copper is not solder coated, a "protective" coating is applied to minimize oxidation of the copper during storage and handling. A good example of a residue problem is the use of a rosin protective coating on a board which is soldered with water soluble flux and cleaned in plain water. Some alkaline saponifier added to the water will help remove this residue.

Water cleaning results in some other residue problems. The surfactants used in the water soluble flux may not dissolve in water that is either too hot or too cold. This is usually not a white residue but the "invisible" residues may be even worse as they are usually conductive. If the alkaline saponifier is too concentrated or too active, the solder on the circuit board assembly can be oxidized. This white or tan residue is not residue at all, but in the right light, it appears to be a film, the film, being tin oxide. Any aluminum fixtures or parts going through the alkaline saponifier will be attacked. The aluminum can be coated with a white reaction product and, in the case of aluminum fixture, the white residue can transfer to the circuit board assembly. The water itself can contain enough cadmium, magnesium or iron salts if harder than 4 grains of hardness to leave a white residue. Even if the water is softened there may be sodium salts that could remain after water washing a circuit board assembly.

Component residues may be material like wax on transformers and capacitors or lubricating oil from switches. These residues are only remaining because nobody considered if they were able to be removed with the cleaning chemicals.

Melted components is not a residue but we have received components or circuit boards with "white residue" problems. Three examples are:-

- A connector with the plastic body made of glass filled polyester. The literature said the connector could withstand 125°C. Of course the leads were being dip solder coated at 250°C. The hot rosin in contact with the plastic was melting it, turning it white.

- A flat pack surface mounted chip carrier was being soldered with a heated bar and solder paste to and epoxy-glass circuit board. The combination of heat and pressure and incompletely cured epoxy degraded the epoxy. This looked like white residue between the component leads.

- Soft plastics such as polycarbonates are attacked by chlorinated solvents. Hard rosin residue is most easily removed with the same solvent. Sometimes the white residue is actually solvent attack on the plastic.

<u>Conclusion</u>

the sudden appearance of white residue on circuit board assemblies after cleaning indicates that something in the soldering/cleaning process has gone out of control. The variety of chemicals, the similarity of materials (rosin vs. resin), the instability of solvents and changing heat could all enter into the creation of white residue. Reactions and stability of the rosin causes most of the residue, but board and component materials can also contribute to the problem.

It is time consuming to evaluate all of the possibilities but quite often a quick chemical test or microscopic examination can determine the nature of the "residue" or in fact, if it even is a residue.