National Physical Laboratory

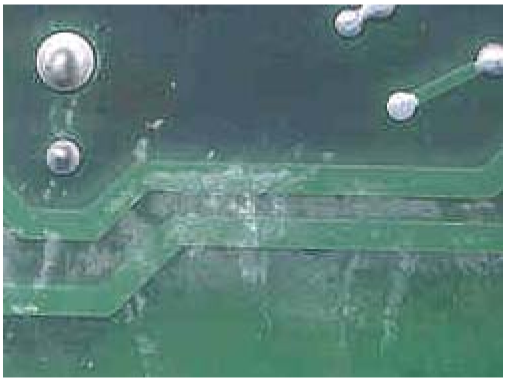
Electronics Interconnection
Free Downloads: www.npl.co.uk/ei

White Residues on Soldered Printed Circuit Assemblies

INTRODUCTION

The investigation into the nature and origin of white residues remaining after cleaning soldered circuit board assemblies has been one of the most common requests to the NPL. Soldering Science and Technology Club. Here we offer a summary of our accumulated experience from troubleshooting and from discussions with other laboratories.

The difficulties encountered in understanding and overcoming the problem arise because the phenomenon is encountered with a wide range of fluxes, cleaning solvents and board finishes, is observed with no known change of process or materials parameters, and the residues are present in such small quantities that chemical identification is always ambiguous with currently available techniques. Superficial investigations reported elsewhere [1-3] have shown that the chemistry of white residue occurrence is complex, and the deposits are of several types and origins.



Generally white residues are translucent surface contaminant films, usually in patches in the vicinity of solder fillets, on assembled printed circuit boards. The residues are insoluble with the commonly available cleaning fluids and cleaning techniques used in the electronics assembly industry. They are usually white but sometimes tinged yellow, blue or grey. The residues are readily visible as a dulling of the board surface and, although normally non-ionic, are a reject condition in most standards because of concern about coating adhesion and long-term reliability of the assembly.

Although normally associated with a combination of rosin-base fluxes and vapour defluxing with chlorinated/fluorinated solvents or alcohol blends, the problem also can occur with water soluble fluxes and with aqueous cleaning of rosin fluxes. Sometimes the residues occur only in the vicinity of solder and sometimes solder is not a necessary requirement. This implies that the nature of the residues may be far from unique and there may be many routes to its occurrence and hence many routes to its avoidance. The soldering and cleaning processes involve so many chemicals in the flux, the solder, the circuit board, the components and the cleaning fluids that a full understanding of the reactions may be unattainable. Invariably the problem of white residues is associated with interdependence between two or more of the materials: the rosin or aqueous salts, the activator, the solder, the cleaning fluid, the laminate, the solder resist.

OXIDISED ROSIN RESIDUES

When rosin is subjected to heat in the presence of air its constituents begin to oxidise at a significant rate. The main constituent of rosin, abietic acid, is particularly susceptible because of the unsaturated double bonds in the molecule. The reaction results in the formation of peroxides and ketocompounds, which are considerably less soluble in solvents than the original rosin. If the oxidation is excessive these products remain after cleaning the printed circuit assembly and are apparent as irregularly distributed white film patches over the surface, more obvious in those parts of the board that have absorbed the most heat. Because of the requirement of excessive heat for this form of white residue to occur, it is most often seen on thick multi-layer boards with ground planes that have required a lot of heat to accomplish soldering.

These white residues cannot be removed by chlorinated or fluorinated solvents, by alcohol or by saponified water except with appropriate scrubbing. However, since like materials dissolve each other, the residues can be dissolved by melted rosin that is best applied as a flux. Any alcohol-based organic acid flux should succeed, but a repeated recoating with the original flux with a gentle heat is easiest. As long as there is sufficient rosin to maintain the oxidised rosin in solution, the entire board can then be recleaned using the normal cleaning method.

POLYMERISED ROSIN RESIDUES

Another source of white residues is often stated as the polymerisation of rosin fluxes during the soldering operation. The polymerisation occurs when excessive heat is used for the soldering and therefore, again it most likely to occur on thick multilayer boards.

When rosin polymerises, some of it becomes very long chain molecules that cannot be dissolved in commonly used solvents. The flux-cleaning solvents dissolve only the short-chain segments and leave behind a tenaciously adherent white film that is the polymerised rosin.

Although polymerised rosin is the most often declared cause of white residues, it is thought that the reaction must be catalysed by, for example, the tin oxide on the solder surface, but even under those conditions, polymerised rosin is not likely to be appreciable in the time and at the temperature available.

The removal method of residues of polymerised rosin is the same as for oxidised rosin, namely to recoat in a excess of flux and then reclean.

HYDROLISED ROSIN RESIDUES

Although pure rosin is practically insoluble in water it will absorb water with a consequent hydrolysation of the constituent acids. The hydrolysed parts of the rosin are rendered partially or totally insoluble in the cleaning solvents. It seems that if the water is saponified the hydrolysation is inhibited, and the problem is rarely caused directly by water washing. Usually the flux during flux storage or the assembly process absorbs the water. Moisture is commonly absorbed from the air feeding a foam fluxer or directly into the alcohol vehicle of the flux. It has been stated unequivocally by one company that their white residue problems are correlated directly with the atmospheric humidity [2].

The hydrolysation of liquid flux is reversible by gentle heating to over 1000C, and so the flux can be dried. Unfortunately the violent high thermal gradient heating associated with the soldering process provokes other complex irreversible reactions of the hydrolysed rosin.

LAMINATE + FLUX + SOLDER RESIDUES

A common type of flux residue is a beige translucent flux residue that is insoluble in halogenated cleaning solvents. The film is normally patchy and thicker close to exposed solder surfaces. The exact formation chemistry has not been established but the film is certainly rosin based and associated with the laminate chemistry. It is probable that a local excess of epichlorohydrin present in the laminate initiates a polymerisation reaction in the rosin flux rending the flux insoluble. This reaction is likely to proceed only when catalysed by tin oxide on the solder surfaces, and hence the solder is a prerequisite.

SOLDER + ROSIN FLUX RESIDUES

During soldering with a rosin flux, the surfaces of the solder and the component terminations can react with the carboxylic acids in the flux to form a class of compounds called metal soaps or tan residues which are virtually insoluble in either water or the fluoro-chlorocarbon range of solvents. A wide variety of compounds form between tin, lead, copper or iron and the acids in the rosin, but it is the tin and lead abietates and pimarates that are most abundant. These arise through reaction of the solder in the molten state with the two isomers of abietic acid, that form some 80% of the purified wood rosin, and the two isomers of pimaric acid that form some 15% of the rosin. These residues are translucent with a yellow-brown tinge to the film. They are associated with solder fillets and solder coated surfaces and so the contamination is found on or in the close vicinity of solder surfaces. The solubilities of tin and lead abietates in four solvents are given in Table 1.

TABLE 1: SOLUBILITIES OF METAL ABIETATES AT ROOM TEMPERATURE (mg/g of saturated solution)

	tin abietate	lead abietate
water	3.2	0.7
fluoro-chlorocarbon blend	40.8	2.2
dimethyl-formamide	207.9	99.0
chlorocarbon blend	275.5	17.1

The lead abietate is considerably less soluble than the tin abietate in all solvents. The salts of pimaric acid are even less soluble in water, alcohols and chlorofluorocarbons. The fluorocarbon solvents are much less useful in removing these residues then the chlorocarbon solvents.

Normally these compounds, as they are being formed at the molten solder surface, are mixed with the flux and are flushed away. However if the flux is unduly oxidised, these organo-metal complexes remain on the surfaces.
It has been suggested [41 from evidence of IR spectroscopy, that the formation of tan residues is a two-step process: heating the flux first produces a pre-cursor chemical species that then reacts with the alcohol in a typical azeotropic cleaning solvent. Tan residue was not found when using an alcohol-free solvent.

Two further methods have been found to eliminate the problem of tan residues. First, by reducing the amount of time that the rosin remains hot, by increasing the wave soldering conveyor speed. Second, by using an oil with the solder wave, which prevents the adhesion of the tan residue.

These types of residues can be identified from others, by their solubility in acetonitrile and tetrahydrofuran. These solvents are flammable and are to be used only in a laboratory, not in production.

SOLDER + HALIDE ACTIVATOR RESIDUES

The halide activators, common in electronic grade fluxes, improve the efficacy of the flux in removing metal oxide films from the surfaces to be joined, and also improve the heat stability of the rosin. In the presence of highly active, hot, clean metal surfaces, these halide activators react to produce metal halide salts, usually tin, lead and copper chlorides. Normally the rosin, with its high electrical insulation resistance keeps these halides dormant but if the halides are not completely removed with the rosin during cleaning, reaction with the solder surface is possible, manifested as a whitish film residue. Most commonly, lead chloride appears, which is insoluble in alcohol and not soluble enough in water to be removed during a water-wash cycle. In the presence of moisture and the carbon dioxide in air, carbonates will form, notably the basic lead carbonate $2PbCO_3 \cdot Pb(OH)_2$ that is also white in colour, totally insoluble in water and in alcohols. The lead, rather than the tin, chloride and carbonates form because the surface of the clean solder is lead-rich since the surface energy of lead is lower than the of tin. In the continued presence of moisture a corrosion cycle is set up since lead chloride plus carbon dioxide plus moisture react to form the carbonate plus hydrochloric acid, which continues to react with the metallic lead in the solder to form more lead chloride. This process occurs more commonly with water-soluble fluxes containing halide activators but can also occur with activated rosin fluxes that have not been completely removed.

To ascertain whether a white residue is associated with halide ions, a piece of wetted silver chromate test paper placed in contact with the residue will turn from brown to white if traces of chloride are present or to yellow if traces of bromide are present.

Thus, in summary, this white residue is lead chloride plus, in the presence of moisture, basic lead carbonate. It is associated with solder surfaces and will turn moist silver chromate paper white. The best way of avoidance is to use a less active flux and either doing no cleaning or complete cleaning of the flux as soon as possible: the problem arises with incomplete cleaning.

SOLDER + CLEANING SOLVENT RESIDUES

A chlorinated or fluorinated solvent used for cleaning flux residues from the soldered assembly can be the source of halide ions that give rise to the same reaction and corrosion chemistry as described in the previous section. The nature of the white residue is again either lead chloride or, in the presence of moisture, basic lead carbonate.

Inhibitors are added to the commercial solvent blends to help prevent degradation or 'souring' but, especially in the presence of flux, and of water from condensation, the solvent can become acidic.

Alleviation of the problem comes by avoiding old or dirty cleaning solvent, and by avoiding moisture condensation into the solvent, usually associated with the vapour condensation coils during turn-off.

LAMINATE + FLUX RESIDUES

A typical thermosetting epoxy resin as used to make FR-4 glassfibre laminate is based on a reaction between epichlorohydrin and tetrabromobisphenol A. The bromine is included for fire retardance. The resin might be incompletely cured either because the laminate manufacturer or the multilayer board manufacturer made a mistake or the resin was misformulated. If the epoxy is undercured the carboxylic acids in the rosin flux react with both the epoxy group and the hydroxyl group to form esters. Esters are generally soluble in alcohols and so are unlikely to contribute to the class of visible insoluble residues. However the brominated phenol in the curing reaction begins to thermally decompose at only 135 0C. Without a complete thermosetting cure of the laminate, at the soldering temperature it is possible for the aqueous chloride ions in the flux to react with the surface, decomposing brominated phenol to produce free bromide ions that react with the lead-rich solder surface to form an white film residue of lead bromide. This is insoluble in alcohol and cold water.

Thus, this residue is lead bromide associated with the areas close to solder surfaces. It can be identified by application of moist silver chromate paper, which will turn yellow in the presence of bromide ions. The residue is soluble in dilute acids. The problem is one of process control by the laminate or multilayer manufacturer

.

AQUEOUS CLEANING RESIDUES

Some instances of white film residues have been identified as peculiar to water cleaning. If the alkaline saponifier is too concentrated or too active, the solder surfaces on the printed circuit assembly can become oxidised. Although in inert atmospheres, lead segregates to an oxide-free solder surface because of surface energy reduction, in an oxidising environment the surface of solder may be almost entirely tin oxide because of the reaction thermodynamics. The tin oxide film is white. It is not a residue but generally is indistinguishable from such.

If the assembly contains aluminium or zinc fixtures or fixtures plated using a phosphorus bearing process, the solder may have become contaminated with these elements that are oxidised preferentially, resulting in an aluminium oxide film, a zinc oxide film or a mixed phosphorus/tin film respectively.

Any aluminium fixtures or parts passing through the alkaline saponifier will be attacked, leaving a white residue on the aluminium that can transfer through the water to the circuit board assembly.

The water itself, if from a hard water supply, can contain enough magnesium, iron or cadmium to produce a white residue problem during the drying stage of the operation. Normally water is blown off the assembly to prevent water-soluble white residues remaining, but this is never perfectly efficient. Even if the water is softened these may be sodium salts remaining on the assembly after water washing.

SCREEN PRINTED SOLDER MASK

Fine alumina powder is frequently added to resin formulations designed for screen-printing, as the particle shapes and sizes can be adjusted to improve or optimise the Theological properties. If a printed solder resist containing alumina is badly cured the flux or the cleaning solvent can superficially attack it. Such an attack need only remove sub-nanometre thicknesses of resin to expose particles of alumina. Within the resin the alumina is virtually invisible but as soon as the particles are exposed they present a clearly visible greyish patchy surface. This fault is not, of course, a residue but is often mistaken for such. A scanning electron microscopy examination will render visible the individual alumina particles.

This visible fault can be removed by using a hot air gun operating at about 150 0C. The surface resin is heated in excess of its glass transition temperature, at which it softens, resubmerging the surface alumina. The problem is avoided by ensuring that the wet ink solder mask is fully cured.

DRY FILM SOLDER MASK

Dry film solder mask can, in principle, can give rise to the same generic types of white residues as the laminate if it is not adequately cured. Dry film solder mask has been often directly implicated in white residue problems when in reality the mask has only an indirect role. This indirect role is because the residue films, formed by a mechanism that is unassociated with the dry film mask, are more tenacious on matt-finish films than on gloss-finish films.

In general, when using dry film solder resist, white residue problems seem to be almost completely avoidable by using a gloss finish.

THE IDENTIFICATION OF WHITE RESIDUES

Preliminary identification of white residues on printed circuit assemblies is by use of a range of solvents, used hot or cold, with or without abrasion, applied very locally. Silver chromate paper is also an aid, as described previously. The dissolution or acidity properties of the residue often give a clue as to its chemical nature.

The analytical instrumental methods available for laboratory identification of white residues can be divided into two classes; the surface analysis techniques aimed at chemically characterising the surface in situ and the analysis methods that require some pre-dissolution of the contaminant into a solvent that is then analysed. The first group, such as x-ray photoelectron spectroscopy, Auger electron spectroscopy, secondary ion mass spectrometry and so on [5] all rely on a probe of x-rays, electrons, ions etc. that interact with the surface such that the emitted x-rays, electrons or ions are characteristic of only few surface atomic layers. These techniques normally require high vacuum, are very costly, are time consuming and require experienced personnel. The second group, such as IR absorption, UV absorption, liquid chromatography [6] etc, rely on changes in solvent properties (eg absorption) as a result of minute quantities of solute. These techniques are relatively inexpensive, fast and automated. They do however require the contaminant to be dissolved away from its host surface. Acetonitrile and water is a common carrier.

Because of the complex chemistry of rosins and synthetic fluxes, for example the great number of isomers of abietic and pimaric compounds each giving rise to different absorption peaks, x-ray peaks etc in an analysis spectrum, it is generally necessary to rely on 'fingerprint' spectra from standard compounds. These normally have to be made up specially.

THE ANXIETY ABOUT WHITE RESIDUES

Concern about white residues of PC assemblies is founded on n perceived or actual problems with the adhesion and long-term performance of conformal coatings, and the degradation of surface insulation resistance in humid atmospheres. The first of these concerns, that of adhesion, either at the time of application or during long service life, appears to have no clear evidence to support it. No work to correlate adhesion strength with contamination level has been carried out, to our knowledge, for the very low contamination levels that are currently achieved, even though visible as a white film.

The second concern, namely of surface insulation resistance (SIR), is a problem of contamination and humidity per se, and not especially associated with visible contaminants. There may be more virulent, yet less visible surface contaminants than white residues. Surface analysis techniques are now readily available for measuring surface contamination levels in a quantitative manner. The problem of white residues is undoubtedly over-emphasised because of the criteria of cosmetic appearance that are used to assess soldered assemblies.

In a recent SIR study [7] the role of persistent flux components was illustrated. Although the initial impedances of the cleaned boards (with no visible residues) were very similar whatever flux was used, during accelerated humidity cycling the loss of resistance, in the long-term, depended on the flux that had been used for soldering. However, even after 10 weeks temperature-humidity cycling (MIL-Std-202F, Method

106E), the SIR values returned to their original values upon drying. An appraisal of the existing literature on this subject highlights several points for study:

(i) Realistic inspection criteria for white residues.
(ii) The need to assess invisible residual contamination.
(iii) SIR studies as a function of flux type and cleaning process.
(iv) Correlation of SIR with field reliability.
(v) Correlation of white residues with conformal coating integrity and with corrosion.
(vi) Acknowledgements

The work described in this paper is the result of many SSTC members requesting our assistance in identifying the causes of white residues. The use of sample boards for destructive examination is gratefully acknowledged. Thanks are also due to several groups within the Laboratory of the Government Chemist for useful advice and practical assistance and analyses.