TECHNICALLY SPEAKING

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Why White Residue Forms on Printed Circuit Boards

The appearance of white residues, on circuit boards, is a recurring problem in the PCB manufacturing industry, and generates many questions and complaints for the Tech Support hotline. When contamination is found on the board, after it has passed through the cleaning step, the customer is likely to assume that the contamination has come from the cleaner they are using. Usually residues form on circuit boards due to problems inherent in the nature of the soldering and the cleaning process, and are not due to problems with the chemical cleaners that are used.

All ITW Chemtronics circuit board cleaners are filtered, to remove any insoluble particulate contamination that might be deposited on the board after cleaning. Most residues are the result of inadequate or partial cleaning and can be eliminated by simply repeating the cleaning step. There is another class of circuit board residue, that derives from more complex chemical reactions between the soldering flux, the cleaning solvents, the soldering process, the board laminate and certain process parameters, such a line speed, soldering temperature. These residues usually cannot be removed with conventional circuit board cleaners, and sometimes cannot be removed at all.

Circuit board residues, which are amenable to solvent cleaning, fall into two broad categories, ionic residues and organic residues. Ionic residues can cause corrosion, if left on the board. Organic residues spoil the appearance of the board and can lead to adhesion problems, if the board must be conformal coated. The nature of the soldering flux used, soldering process and cleaning parameters, and problems with the cleaning solvents used, can all lead to the formation of ionic residues. Organic residues can occur due to improper soldering or cleaning techniques or because of a mismatch between the flux and the specific flux remover employed.

It's easy to determine the type of contamination you have on the board. Test each patch of residue with drops of water or alcohol (IPA). If the drops of water dissolve the residue, its ionic; if dissolved by the alcohol, the residue is organic. This quickly tells you what it will take to clean the board (either a water-based cleaner or a solvent-based cleaner), and can give you some indication of what is causing the problem. In both cases, it's more likely to be improper techniques or incomplete cleaning that causes the contamination problem.

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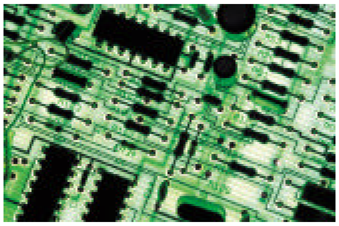
Ionic contamination often results from the type of soldering flux used. Rosin and rosin-based no clean fluxes and many water-soluble fluxes contain varying amounts of halide acid activators. These activators give the fluxes greater heat stability, and help promote the formation of good solder joints by dissolving the oxide films contaminating copper, lead and tin surfaces. The chemical reaction of chloride and bromide ions in these activators, with the lead in the solder, can cause the formation of white lead chloride and lead carbonate residue around the solder joints. If not completely removed during cleaning, these ions can establish a continuing corrosion cycle, producing more lead chloride and lead carbonate (white residue) and hydrochloric acid, which will attack the copper in the board laminate. The best solution to the formation of ionic contamination is the clean the board thoroughly, as soon as possible, after soldering. Ionic residues can also be removed from the board by cleaning with a water-based alkaline cleaner, such as Flux-Off® Aqueous. Process parameters such a pre-heat and soldering temperatures, along with the line speed can also lead to residue formation. If the line speed is too fast, it does not allow the board to cool sufficiently before it enters the cleaning process. The hot board surface can cause the cleaning solvent to evaporate too rapidly. If using a water-based saponifier like Flux-Off® Aqueous, the rapid loss of water can precipitate other cleaner ingredients, such as silicates and carbonates. This contamination appears as crusty patches on all areas of the board. Slowing the line speed down, to allow the boards to cool sufficiently before exposed to the cleaner, can eliminate this cause of contamination.

Organic rosin residues can arise from a number of circumstances. Using old solvent, that has been stored for some time, can lead to incomplete cleaning. Isopropyl alcohol is used extensively in the industry, as a flux remover and general circuit board cleaner. 70% IPA or "rubbing alcohol" already contains 30% water, and even 99% anhydrous alcohol is hydroscopic and will absorb water from the air during prolonged storage. Diluted IPA is a poor solvent for rosin-based fluxes, and will not dissolve heavy contamination without lengthy exposure time. Also the water in the solvent can react with no clean fluxes, leaving a white residue on the board.



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In hand soldering operations, there is a general tendency to use too much flux solution, leading to a heavy build-up of contamination, which is not easily removed with a single pass through the cleaning process. Repeated runs through the cleaning line will eventually remove this built-up residue. Using too much flux can also lead to flux solution being trapped underneath components. Cleaning must be performed in a manner that flushes this contamination from underneath the components; otherwise partial removal will result in rosin contaminant draining across the board after initial cleaning has been completed. Increasing the residence time of the board with the flux remover can prevent this from happening.

A general mismatch of the cleaner to the contamination type can be inferred by examining how the contamination coats the board. If the areas of residue are patchy in nature, then incomplete cleaning is indicated. Increase cleaning time and/or temperature. If the contamination appears as an even layer over the board surface, then you are not using the right cleaner for the residue present. Cleaners containing HCFCs, like Electro-Wash® PN and Flux-Off® No Clean, will not attack synthetic no clean fluxes, and may even react with the flux, causing the formation of white residue. Usually this type of residue can be removed by using an aggressive cleaner like Flux-Off® Heavy or Flux-Off® No Clean Plus.

Detergent saponifier cleaners, like the Flux-Off® Aqueous ES132, can attack the surface of the solder joints and form a layer of lead and tin oxide film, if the cleaner is used in concentrated form. This is why we recommend that the ES132 be diluted as much as 1:10 with water, for most applications. Flux-Off® Aqueous will also attack metals such as aluminum, and metal-plated surfaces that contain phosphorus, leading to residues of lead and tin oxide or a phosphorus/tin oxide film. These white residues can be transferred to the circuit board during the cleaning process. Masking such metal surfaces, prior to cleaning, will eliminate the formation of these residues.

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Cleaning: It's All In Finding The Right Balance

A number of factors must be considered when removing contaminants from the surfaces of printed circuit boards and electronic equipment. Finding the proper balance between these factors will greatly improve the speed and efficiency of the cleaning process. Selecting the proper cleaner for the soil type to be removed and compatibility with the surface to be cleaned, selecting the proper cleaning method, finding the right mix of cleaner concentration, temperature, residence time, and cleaning action, are all criteria that must be taken into account when designing the most efficient and cost effective cleaning process. Further complicating the picture is the need to consider solvent toxicity, in relation to worker exposure and safety, and the requirements of local environmental regulations, concerning air emissions and disposal of waste products.

First, consider what type of soil needs to be removed from the surface of the equipment or circuit board. This will immediately suggest the best cleaner to be used for the job. If the surface is covered with light dust and particulates, then an Ultrajet® duster will suffice to remove these loosely bound contaminants.

If the contamination to be removed is ionic in nature (flux residues, inorganic salts, acidic materials) then you will need to perform the cleaning using a product containing **polar** solvents, like water or alcohol. If **non-polar** substances like oil and grease are present on the surface, further trapping dust and particulate matter, then it will be necessary to choose a **non-polar** solvent cleaner to dissolve the oil and grease and flush away the bound particulates. Non-polar solvents like isohexane and other hydrocarbon-based cleaners are good solvents for dissolving non-polar oils and grease. Many Chemtronics solvent cleaners contain both polar and non-polar solvents, so they will be effective on all types of contaminants. Electro-Wash® PX, the Mighty Liquid™ and the new fluorinated solvent mixtures, like Cirozane® and Verizane®, are outstanding cleaners for both ionic and nonionic soils.

Along with matching the cleaner to the type of contamination to be removed, you also need to consider if the cleaner is compatible with

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the surface material being cleaned. You would not want to use a strong, aggressive cleaner on a painted surface, for fear of removing the paint. Likewise, plastic surfaces can be effected by some of these same. solvents. Cleaners containing strong ketones, like acetone, or chlorinated solvents, like methylene chloride, will lift the paint from metal surfaces or melt soft plastics like polycarbonate and polystyrene. The surface of harder plastics can be discolored or "crazed", developing fine cracks and abrasions, when exposed to ketones and chlorinated solvents. The "Xtra Strength" Chemtronics cleaners, like Electro-Wash® NX, NXO and Flux-Off® Heavy Duty should be tested for compatibility with any plastics present in the cleaning application, before widespread use.

Next, consider what is the fastest and cheapest way to do the cleaning? If the decision is made to use a solvent cleaner, then we need to consider whether to use an aerosol product or a bulk liquid. If only a few boards are to be cleaned and the cleaning takes place infrequently, then it is probably less costly and more convenient to use an aerosol product. If many boards are to be cleaned, then using a bulk liquid cleaner may be more cost effective.

In some situations, the concentration of the cleaner being used is also a consideration. Solvent-based cleaners like the Electro-Wash Cleaner/Degreasers and most of the Flux-Off® Flux Removers are not dilutable, and can only be used full strength. **Water-based** cleaners, like Flux-Off® Aqueous, are usually sold as concentrates and can therefore be diluted with water to the concentration that is found to give the best cleaning. For Flux-Off® Aqueous we recommend that the user first dilute one part of the cleaner with 10 parts water, as a starting point for determining the best cleaner concentration. Being able to dilute the cleaner also has the advantage of lowering the cost of the cleaning process.

If you are trying to remove a thick coating of rosin flux, oil and grease, or stripping a conformal coating from the whole board, then its best to increase the **residence time**, that is, the time the soil is exposed to the cleaning solvent, by immersing the board in the cleaning solvent.

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Immersion cleaning can be done at **room temperature** (sometimes referred to as cold immersion cleaning) or, in some cases, a heated bath. **Heating** the cleaning solution will greatly increase the speed at which it works. Of course, only those solvent cleaners with **flash points** above 200 ºF (consult the product MSDS) should be heated, to avoid the possibility of igniting flammable vapors. **Agitation** or stirring
the cleaning solution during immersion adds mechanical action, which can also speed up cleaning. Similarly, such cleaning can be performed in an ultrasonic bath, if available. Transmitting sound waves through the cleaning solution produces fine bubbles (cavitation) which "scrub" the surface of the board. Some ultrasonic baths also allow you to heat the cleaning solution, further increasing cleaning efficiency.

Encrusted soils lying under components are especially hard to remove. If the residence time in the cleaning solvent is too short, the solvent does not have sufficient time to penetrate under the components. There will be only a partial dissolving of the trapped residue, some of which will flow across the board. As the solvent cleaner evaporates, this partially dissolved residue will precipitate onto the board, leaving streaks of soil across the board surface. This is an indication of "incomplete" cleaning , and is easily solved by running the board back through the cleaning process, as many times as required to completely flush all soils from underneath the components. In an automated cleaning process, the speed at which the boards pass through the cleaning process can be decreased to allow the boards a longer time of exposure to the cleaning solution.

To sum up all the above information, proper cleaning of an equipment surface or electronic assembly requires finding the right balance between the variable conditions of **cleaner-contaminant/substrate compatibility**, **cleaning method**, **cleaner concentration**, **residence time**, **cleaning temperature**, and **agitation**. All cleaners will not work equally well with the same types of soils, in the same types of cleaning equipment and processes, or in the same amount of time. Each cleaner has its strengths and weaknesses and finding the right balance of the above factors, for the particular cleaner being used, will result in developing the fastest and most cost effective cleaning method for a particular application.

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More Specifics on Soldering Flux

We've discussed soldering flux earlier, with regard to desoldering the new lead-free solder alloys. We talked of how the flux aids in the soldering/desoldering process by removing oxide films which form on the surface of metals being soldered, how it increases the wetting ability of the solder, causing it to flow more uniformly over surfaces without balling-up. In terms of desoldering braid I pointed out that flux is vital for the formation of the solder-to-braid bond, which pulls the solder from the surface of the PCB; without the presence of flux this solder-to-braid bond would not form and the bare copper wire would not remove any solder.

What else can we say about solder flux? The most basic soldering flux, one that has been used for over a thousand years, is the natural rosin derived from pine tar resin. Pine tar **resin** is dissolved in solvent and then distilled to yield the clear, water-white **rosin** used in soldering flux. Rosin is a collection of naturally occurring acids, chiefly abietic acid and its homologs. When used as a soldering flux, the clear rosin is dissolved in a solvent, usually isopropyl alcohol. When used in this manner, without the addition of acid activators, it is referred to as Type R Rosin flux.

Activators are added to soldering flux to increase the ability of the flux to dissolve heavier oxide films, especially those produced at the higher soldering temperatures required for lead-free solder alloys. Activated fluxes can be either mildly activated or Type RMA (rosin –mildly activated) or RA (rosin-activated). Activators commonly used include organic acids, halogenated (containing chlorine or bromine) compounds, amides, and monobasic and dibasic organic salts. All of these activators are corrosive and should be removed from the circuit board to ensure long term reliability.

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Activated and mildly activated rosin fluxes can leave behind chloride ions and other corrosive residues and therefore must be removed from the printed circuit board after soldering or desoldering to prevent long term corrosion related failures. The residues of these fluxes are also sometimes tacky and attract dust which may contain conductive elements that can cause shorts and other electrical failures on the board. As lead-free solder alloys become more prevalent in manufacturing, the use of highly activated fluxes, to overcome oxidation film formation at higher soldering temperatures, will increase. Thorough cleaning after soldering or desoldering, when using a lead-free alloy, will become mandatory.

No Clean fluxes can be either made with natural rosin, or contain synthetic resins. Rosin-based No Clean flux solutions are essentially the same as the rosin (R Type) fluxes, but usually contain natural gum rosin at a much lower concentration than that used in the R Type (R, RMA and RA) flux solutions. True synthetic No Clean fluxes contain synthetic resins that impart the same desirable properties to the flux as does the natural rosin product. No Clean flux solutions can also contain additional activators, and the residues they leave behind can lead to corrosion.

No Clean fluxes were designed to help circuit board manufacturers skip the time and expense of cleaning the board after soldering. No Clean fluxes leave much less residue behind than the conventional R Type flux, and this smaller amount of residue will usually not interfere with the operation of the board or cause long-term corrosion-related failures. The residues left by a No Clean flux may be sticky and attract dust or otherwise detract from the appearance of the circuit board and therefore can require removal (cleaning) to meet appearance or operation standards. If the circuit board is to be conformal coated to protect the circuitry during operation, the board surface must be free of flux residues, even the minimal residues left by No Clean flux, to ensure good adhesion of the conformal coating. The need to use more activated (corrosive) flux when soldering with lead-free alloys may also make removing flux residues a necessity, further reducing the benefits of using No Clean fluxes.

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Water soluble fluxes usually employ water-soluble resins whose residues should be removed using a water rinse. Some water-soluble fluxes are water-based solutions, which eliminates the need for using an alcohol-based flux solution. This is one way in which VOC emissions can be reduced, for those board manufacturers operating under stringent environmental regulations. Acid activators commonly used in water soluble fluxes include organic acids, halogenated (containing chlorine or bromine) compounds, amides, and monobasic and dibasic organic salts. All of these activators are corrosive and should be removed from the circuit board to ensure long term reliability.

The IPC J Standard (Joint Industry Standard) flux classification system has replaced the military's soldering standards under QQ-S-571 and MIL-F-14256.. Fluxes are rated as RO (rosin), OR (organic), IN (inorganic) and RE (resin/synthetic resin). The activity of the flux solution is rated as L (low activity or <0.5% halide), M (medium activity or 0 to 2% halide) and H (high activity or 0 to >2 % halide). Fluxes are classified for halide (Cl^- or Br^-) content as 0 (no halides) or 1 (some halides). The Under this classification scheme an ROL0 flux would be a rosin flux with low activity and zero halides An RMA flux could be classified under this scheme as an ROM1, if it contained 0.5 to 2.0% halide content.

As a side note, the flux used on all Chemtronics desoldering braid, for both Chem-Wik® and Soder-Wick® braid, is lead-free. Likewise the CircuitWorks® rosin-cored Pocket Solder, part number S100, and the two CircuitWorks® flux dispensing pens, part numbers CW8100 and CW8200, contain lead-free flux components.

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