

VOC-free fluxes and solder balls

By

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Introduction

Probably not even Bell & Zajitschek realized how strong the prophecy was in their final statement in "The Solder Ball Problem, Research and Results". In August 1994, they wrote: "We are aware of the fact that, due to the rapid development in the area of electronic circuits, new demands will be made upon materials and process technology. Demands that will cause a revival of the solder ball issue"¹. This was at almost the same time when the so-called VOC-free flux technology was breaking ground in the US electronics industry.

Background

It was in the early nineties that The South Coast Air Quality Management District (SCAQMD) in Southern Californian spearheaded the US-restrictions on the usage of materials containing VOC's. VOC's are volatile organic compounds with a vapor pressure higher than 0.1 mm Hg at 20 °C under California guidelines. The alcohol in traditional wave-solder fluxes fall into this category. VOC's potentially contribute to the formation of smog, global warming (the greenhouse effect), as shown in figure 1, and ozone near the ground. So environmental conditions as well as public health and well being are in jeopardy when no restrictions are enforced.

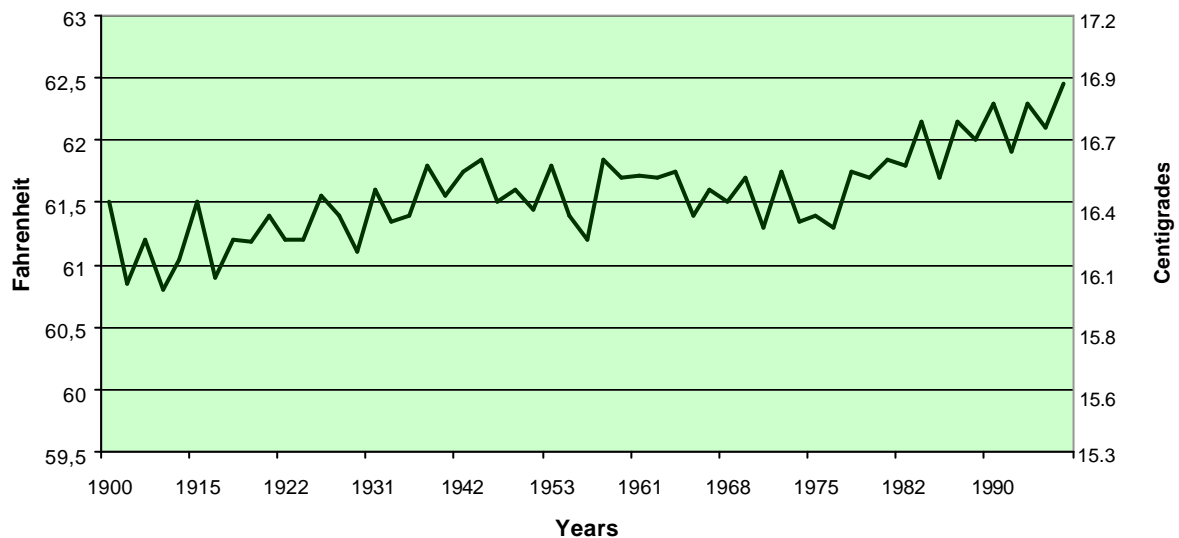


Figure 1: The temperature trend over the last 100 years is seen as proof of global warming by many scientists. 1997 was the warmest year of the century. The diagram shows average global surface temperature for each year, a combination of both land and ocean surface readings. Source: National Oceanic and Atmospheric Administration (USA).

In 1997 the Kyoto Conference on environmental issues agreed on a protocol for the reduction of VOC-emissions by the year 2010 with commitments for the US by 8%, Japan by 6% and the European Union by 7%. The objectives per country in the European Union are listed in table 1. The media exposure on this issue has created some political awareness worldwide. This, in conjunction with the drive of US-corporations to make the VOC-free flux technology part of their green-image concept worldwide, has resulted in a more global interest in this issue.

Commitments for cutting greenhouse gasses by the European Union

	%		%
Belgium	-7.5	Luxembourg	-28
Denmark	-21	Netherlands	-6
Germany	-21	Austria	-13
Greece	+25	Portugal	+27
Spain	+15	Finland	0
France	0	Sweden	+4
Ireland	+13	UK	-12.5
Italy	-6.5		

Table 1: The global warming treaty approved by the Kyoto conference in 1997 requires the US and other industrialized areas to cut back on their emissions of carbon dioxide, methane and other heat-trapping greenhouse gasses. The European Union has struck a legally binding deal to reduce its output by 8% by the year 2010. The table however shows distinct differences per country. Source: UK government.

The attention paid to issues related to ISO-14001, The environmental Assurance System, in countries like Taiwan and the enforcement of the restrictions on the emission of VOC's in Scandinavia and other areas in Europe will contribute to the global interest in VOC-free flux technology.

The basic chemistry of VOC-free fluxes

Although technically one could consider organic solvents that are exempt of the EPA-definition as a VOC-material, water still is first choice to replace the VOC's in a wavesolder flux. It is the most natural, yet the most powerful vehicle to support the ion mobility of the activators. Water however has a significantly different surface tension. The latter requires property-modifying additives to avoid beading of the flux, once applied to the board-surface. Furthermore some activators and many film-forming polymers used in alcohol based fluxes are not - or only sparingly - soluble in water. Therefore different materials had to be used in the development of water based No-Clean fluxes. Those materials do not have the same track record with regard to circuit integrity. Some flux-formulators simply selected some readily water-soluble materials. With a self-proclaimed leadership and a media-hype they introduced the product into the market without proper verification of neither the performance nor the reliability of the product concerned.

The benefits of VOC-free fluxes

VOC-free fluxes eliminate the following issues:

- * Process control problems due to solvent evaporation
- * Thinner consumption
- * Waste disposal problems
- * Ozone - Nozone discussions
- * Smog concerns
- * Greenhouse effect considerations
- * Fire risk
- * Restrictions and extra costs for transport, storage and handling

Figure 2.

Will solder balls make VOC-free fluxes lose their face?

In 1995 a leading German automotive electronics manufacturer rejected the VOC-free, No-Clean process after a careful evaluation of the fluxes available at that time. The process was not qualified because of inadequate dielectric properties of the residues and the number of solder balls found on the soldered assemblies.

Other companies, who voluntarily evaluated the process, had similar experiences.

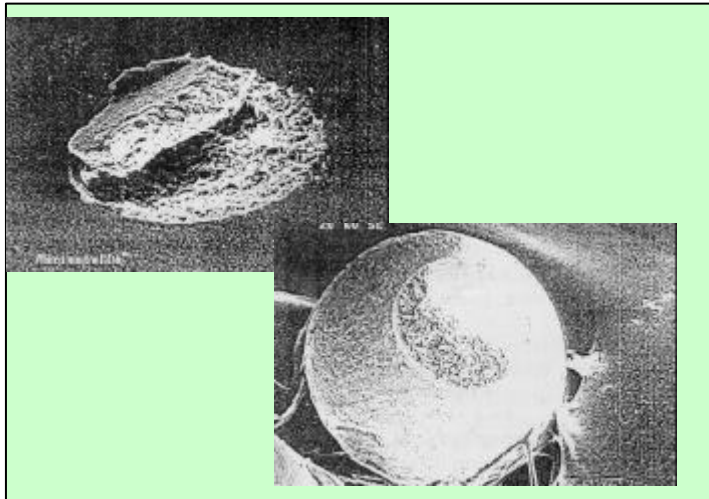


Figure 3: Systematic solder balls in general adhere firmly to the solder resist. Upon removal the contact area quite often shows 'craters' in the resist as well as on the solder ball. EDX-investigations show that exchange of elements has taken place through chemisorption. Pictures courtesy Bell & Zajitschek.

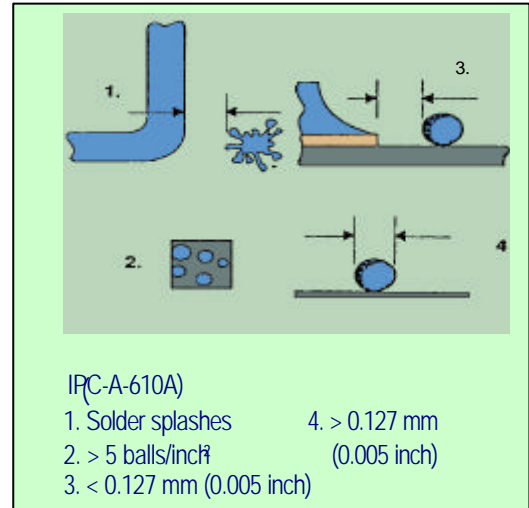


Figure 4: Several international standards specify the criteria for the acceptance of solder balls.

Moreover, the idea developed that in the US traditionally wavesolder equipment had longer preheat zones to handle both higher process speeds as well as the specific chemistry of water-soluble fluxes. The extra preheat capacity helps to volatilize the water in VOC-free fluxes.

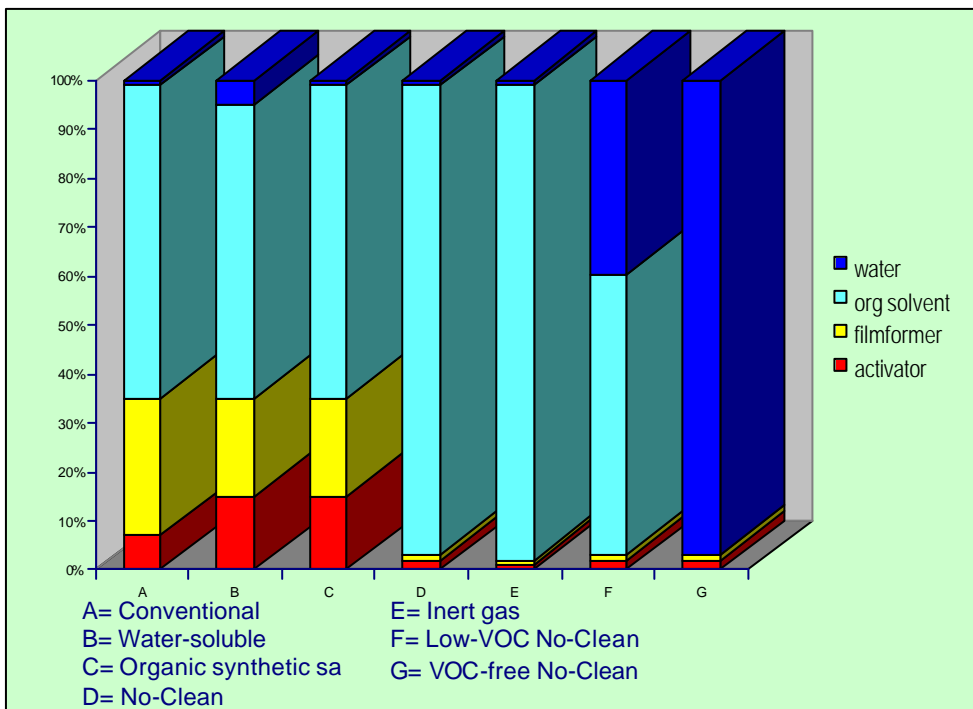


Figure 5: The main stream in the historic developments in solder flux technology over 4 decades visualized. The changes in solids content and the replacement of wood rosins by modified rosins and synthetic filmformers have been driven by the No-Clean concept. The replacement of alcohol and other volatile organic solvents by water are caused by the call for VOC-free technology.

In other parts of the world quite often existing wavesolder equipment has lower preheat capacity and therefore creates an extra stumbling-block for the acceptance of VOC-free flux technology. By now it has become a common perception in the industry that commercially available VOC-free, No-Clean fluxes create problems meeting reliability criteria as specified in international standards such as Bellcore. Moreover, when using this flux technology one has to accept a significant increase in the ratio of solder balling².

For most applications the latter is not acceptable. So many of the companies who are not forced yet by legislation to reduce their emissions, still prefer to continue with alcohol based fluxes. In the US-industry many assemblers cannot return to alcohol based technology and therefore some had to re-adopt post-solder water cleaning in order to remove the solder balls. For cost-competitive reasons this, however, is only accepted as a temporary compromise.

When we, at Cobar's Technical Headquarters in Breda, Holland embarked on a program to develop technology that would result in VOC-free, water-based solder fluxes that would both eliminate solder balls and be certifiable to the Bellcore standard by an internationally accepted, independent laboratory, we considered the work of Bell & Zajitschek as our reference. They spearheaded a task force on 'solder-balls' that worked for several years and included members representing the interest of board-assemblers, board manufacturers and suppliers of solder-resist, wave-soldering equipment and flux vendors. Therefore their work may be considered as the most unbiased, the most fundamental and based on a multi-disciplinary input.

According to Bell & Zajitschek of all parameters impacting the number of solder balls on a soldered assembly, more than 50% is related to the nature and the properties of the solder resist. The solder flux is the second most significant factor with 17% (See figure 5).

We were interested to verify whether or not at the present state-of-art in solder flux technology, the solder resist still is significantly more important with regard to the elimination of solder balls. In particular the ability of VOC-free solder fluxes to eliminate solder balls was the focus of this program.

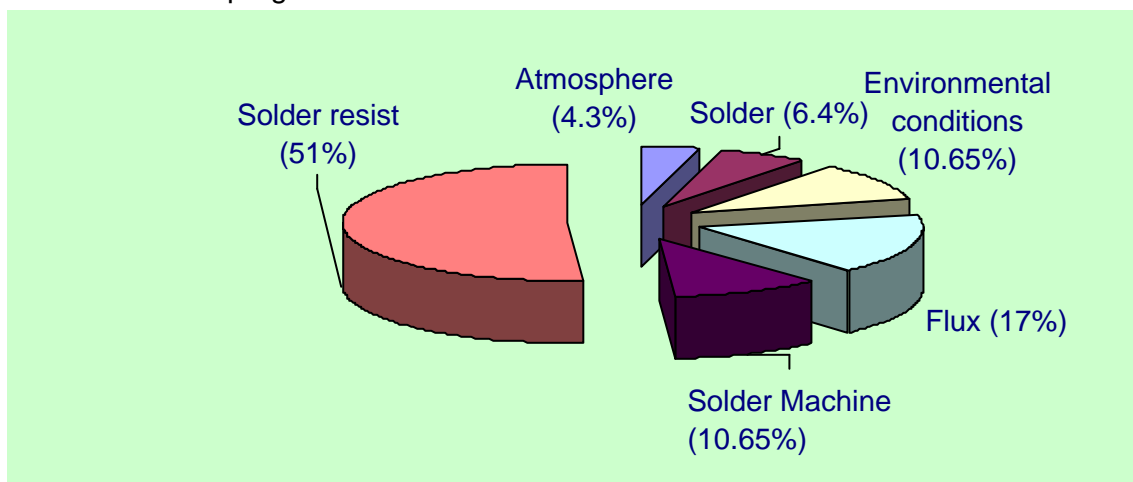


Figure 6: The relative contribution of individual parameters to the formation and adhesion of solder balls according to Bell & Zajitschek, based on the state-of-the-art technology up to 1994. Today the weight of properly developed flux technology is significantly greater.

The role of surface chemistry in VOC-free fluxes

For many reasons surface chemistry is of paramount importance to VOC-free fluxes. First of all the flux should start wetting and spreading into a uniform and continuous film all across the surface of the circuit board immediately after its application. A flux that beads up

immediately after its application and does not spread out into a thin continuous film, requires more preheat energy to evaporate the water. Also the flux must exhibit sufficient bonding strength to the surface of the circuit board so the wet film is not instantly blown off by the airflow in the preheat-zone. Furthermore it is obvious that the flux should cover the entire board, so the activators are evenly distributed in order to arrive at a perfectly soldered board.

In order to arrive at the synthesis of the proper surface chemistry for VOC-free fluxes, we must consider that successful wave soldering of circuit-assemblies requires not only perfect wetting of metallic parts but also perfect de-wetting of non-metallic parts.

Although this may seem obvious, it definitely cannot be taken for granted. The difficulty that the industry has experienced with solder balling on resist surfaces is graphic proof that de-wetting of the resist surface is not a trivial consideration¹.

So, apparently it not only is necessary to deliver the activator systems smoothly and reliably to the metallic surfaces, but it is also important to insure that the molten soldermass smoothly, reliably and completely parts from the non-metallic when the board exits the wave.

Considering the fact that the properties of the solder resist are an important parameter, it is evident that a closer observation of its functionality is of paramount importance. The solder resist, so often thought of as an inert chemical barrier preventing contamination of the board surface is, in fact, often far less inert. During the circuit-board fabrication process the resist can act like a sponge absorbing and adsorbing various chemical species it comes in contact with. These species can be released during soldering, dramatically changing the soldering environment, and modifying the surface state of the solder resist.

Adsorption of the flux onto the surface of the solder resist should be initiated without delay so the flux can interface with or dissolve the chemical species (contaminants) that may have penetrated during the board manufacturing process, storage, assembly operation, etc.

The solder flux also must exhibit a highly controlled surface energy during the time it is in contact with the solder wave. It must rapidly spread on the entire surface, displace the contaminants, and build a uniform monomolecular film, which prevents the proper surface energy profile to the wave. This is done using a very particular blend of surface active materials whose characteristics have been optimized for the acid environment of the solder flux and the heat profile of the solder process.

Surface tension considerations alone are not enough to give us a complete understanding of this phenomena. Surface energies are also very important. For our monomolecular film to be stable it must not only wet the surface, but also it must be adsorbed on the surface in a stable configuration during the very high temperature excursion through the solder pot. This implies a strong charge binding mechanism, also during that phase of the soldering process.

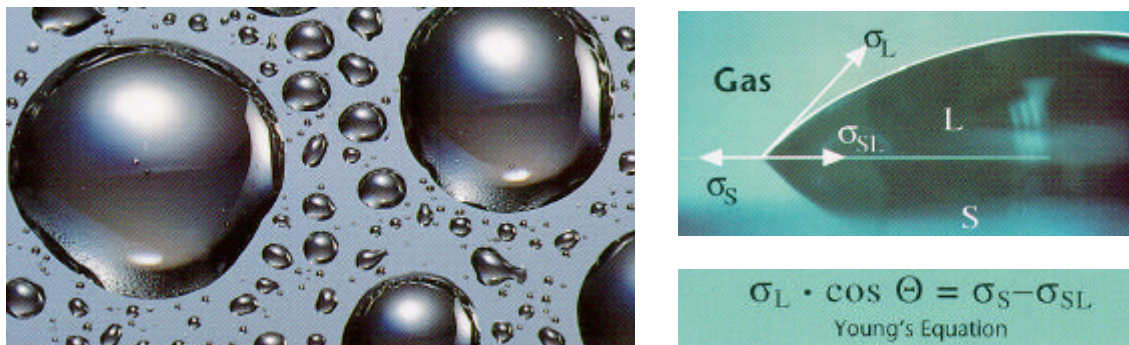


Figure 7: The left picture shows beading of a water-based flux on a glass substrate immediately after its application by spraying. An improper system of surface-active material prevents the spreading into a continuous and uniform film across the surface. The flux remains in droplets having an increased contact angle as visualized in the left picture. The Young equation (bottom right) provides the basis for the determination of the surface energy as a measure for the probability of the formation and adhesion of solder balls.

As with most other functionalities in chemistry there is no such thing as the ideal universal surfactant suitable to meet all requirements and compatible with all the different morphologies. Quite often a combination of several surfactants (from different categories) is required to both control the surface tension and the interfacial tension at the solid-liquid interface.

The objective with a properly designed system of surface chemistry as an essential part of a wave solder flux is

- 1) improved wetting of the flux on the non-metallic areas
- 2) low surface tension in conjunction with low interfacial surface tension yields instant spreading of the flux over the various surface morphologies.
- 3) better penetration of the flux via absorption into the subsurface of the solder resist.

The force and time required to penetrate into small pores can be significantly reduced.



Figure 8: Different solder resists result in different surface morphologies. The picture in the left shows a relatively smooth surface. The surface in the middle picture shows a relatively rough surface with pores up to 4 microns. The right picture shows the edge of a solder resist. These images underline our theory that the solder resist is not a chemically inert, non-porous film. It is capable of soaking up and retaining a substantial amount of process fluids during the board manufacturing process. Pictures courtesy Bell & Zajtischek.

Efficient adsorption and absorption of a surfactant are only possible if there is a strong bonding potential between a specific surface morphology and a particular surfactant. Obviously different surfaces have different morphologies yielding different surface energy states and it cannot be expected that a single type of surfactant will interact with all types of surfaces. Advanced surface chemistry in a No-Clean wave solder flux utilizes a range of chemically different surfactants at carefully tuned, relatively low, ppm ratios to interact with many types of different morphologies. Many surfactants perform better and in a more universal way when they can work synergistically with other carefully selected surfactants.

A properly designed surfactant system will not only assist in the repulsion of the hot liquid solder mass from the non-metallic areas, thereby reducing the occurrence of solder balling. It will also improve the performance in the application of the solder flux.

Surfactants will control the droplet size of the flux upon spraying which is essential for a controlled distribution of the flux and sufficient capillary activity in vias and thru-holes. Surfactants will reduce the bubble size of gasses escaping from the pores of the solder resist when exposed to the solder wave.

Additions in the low-end ppm range of an advanced and well designed system of surface chemistry will contribute to higher SIR and reduce and in many cases eliminate the problems of solder balling and assist in a uniform heat transfer during the wave solder process.

High ratios of surfactants would create more cons than pros:

- * more residue
- * uncontrolled spray applications
- * reduced SIR values
- * increased costs

Also, the surface chemistry in wavesolder fluxes should not jeopardize, but preferably improve the dielectric properties of the assembly after soldering. The surface chemistry needs to survive the process to such an extent that it can perform the task it has been formulated for.

The development of a 'solder ball free', VOC-free flux

Based on these assumptions a program was set up to develop VOC-free flux technology that would prevent the incidence of solder balls. Amongst many other requirements our preliminary design specification stipulated the development of a water-based product with the lowest amount of VOC's, the lowest solids content, the lowest acid number and the lowest, yet most powerful ratio of surface active materials.

The first step was the prototyping of a blend of surface active materials in a water-based system, that would provide the largest possible 'interface window' for the - potentially - numerous surface morphologies of the solder resist. The latter being caused not only by the differences in the type of materials, but also by the tolerances caused by the board fabrication process. The objective was to tune the blend so it would do its job to prevent solder balls on one hand, but to minimize the total amount of surface active material to avoid uncontrolled accumulation of materials in the flux. The latter would impact the surface insulation resistance and other properties related to circuit integrity.

The performance of various prototypes and some commercially available VOC-free fluxes, - marked as A, K, M and Q - was evaluated. We soldered a statistically acceptable number of surfaces ranging from glass plates coated with a 2pack liquid photo-imaginable resist to boards with dry film resists. The runs with the coated glass plates were recorded with a high-speed video camera sitting over the solderwave. The latter enabled us to study the differences in turbulence in the solderwave and the impact of the flux on the outgassing of process fluids from the solder resist.

Solder ball count

average number of balls/board

	A	B
396-RXM	0	1
A	9	11
M	12	15
K	7	13

A = liquid resist
B = dry film

Table 2: Solder ball counts on glass-plates and FR-4 material with various solder resists.

Solder ball counts on all test samples were carried out using a stereomicroscope with a 10 x magnification and a Hiroc microscope with a rotating imaging angle. The physical properties of some of the samples are listed in table 3 and some results on the solder ball count are listed in table 2.

Physical properties VOC-free fluxes

	396-RXM	A	M	K
SG at 20 C	1,006	1,090	1,006	1,060
Acid Number	15,35	32,50	16,25	18,00
Solids Content	1,95	4,00	3,25	2,00
Halide Content	none	none	none	none

Table 3: Some physical properties of the VOC fluxes that have been tested. All data have been taken from the sales specification, except for the SG. This value was verified by accurate determination at exactly 20 °C, as this value is important input for the precise determination of surface tension.

Test boards of all runs were evaluated for ionic contamination, measuring the post-solder residues in terms of NaCl equivalents (Table 5).

Ionic contamination

micrograms NaCl /cm

	A	B
396-RXM	0,31	0,37
A	0,98	1,01
M	1,25	1,34
K	1,17	0,99

A = liquid resist

B = dry film resist

Table 4: The ionic contamination on the boards soldered with the test-fluxes was measured using a Protonique Contaminometer.

Using instruments according to the Wilhelmy-Plate method and the Pendant Drop method the static surface tension of the fluxes at 20 °C was determined (Tables 5 & 6). There is a significant difference in static surface tension of the fluxes investigated by both methods. There also is strong correlation between the results of both methods but - as expected - there is no correlation between the static surface tension of a flux at 20 °C and the frequency of solder balling.

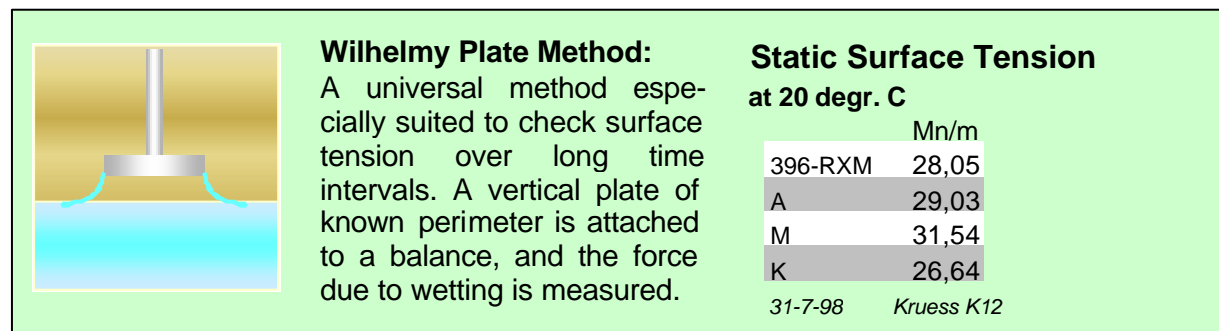


Figure 9: Static Surface Tension determined in 2 decimal places at 20 °C, using the Wilhelmy-plate principle.

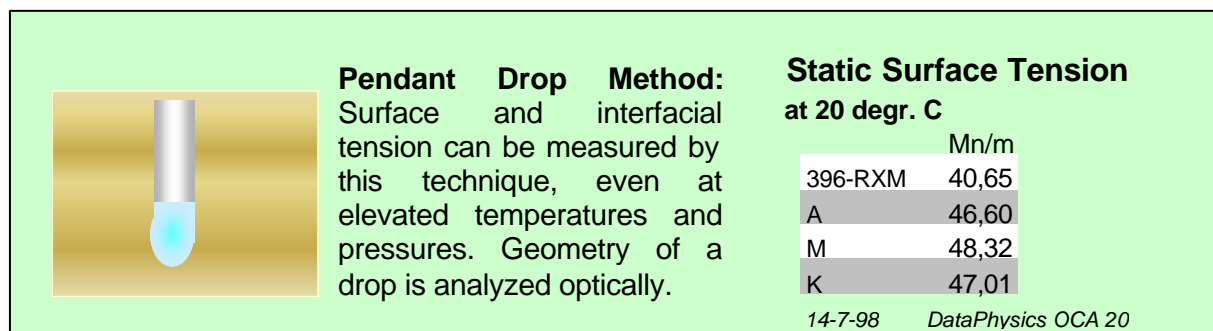


Figure 10: Static Surface Tension determined at 20 °C with the Pendant Drop method. Note the correlation with the results of the Wilhelmy-Plate method

The performance of a flux in a dynamic process of spraying, the wetting, adsorption and absorption of the product during the preheat phase may be determined by the speed of the surface active species influence the interface with the solder resist.

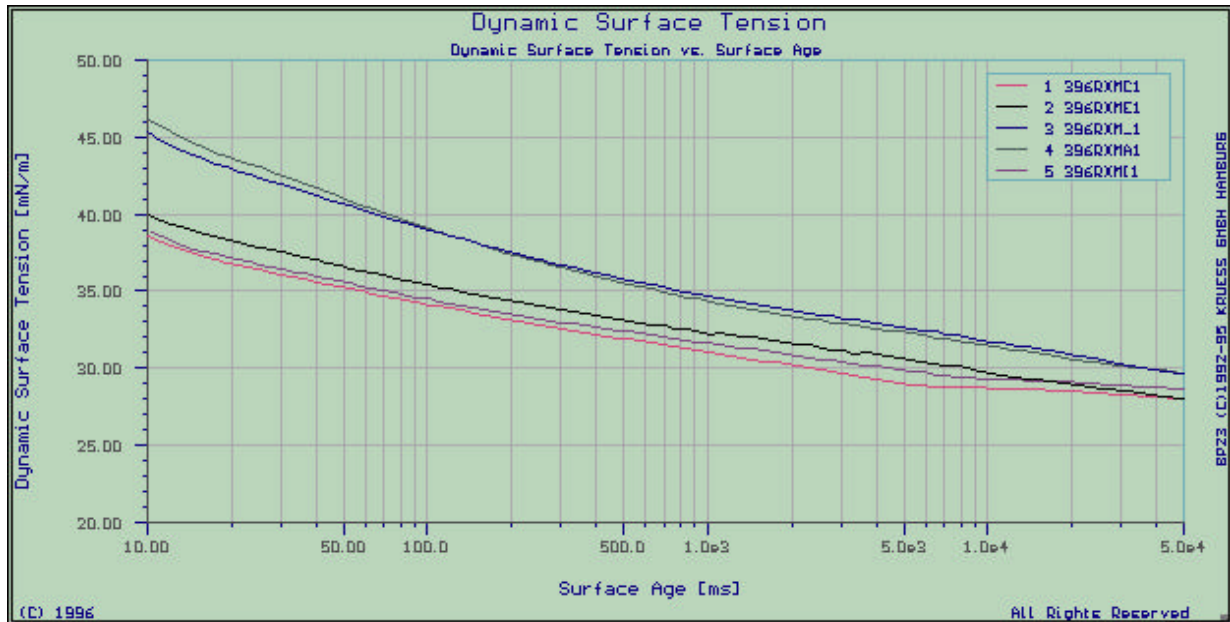


Figure 11: The dynamic Surface Tension at 20 °C with the Bubble Pressure Method. This is a study of several prototypes differing in variations in the blend of surface-active material. The prototype in curve 5 contains five times less the quantity of the same material than the formula in curve 1. Pruning back the deadwood in the blend of surface active materials and at the same boosting the performance of the blend by taking the advantage of the synergy by adding some quantities of a considerable number of other materials in the low-end PPM range were the objectives of the study.

The dynamic surface tension of a solder flux therefore might provide a measure of the kinetics of surfactant adsorption and orientation. Therefore we also characterized the fluxes by their dynamic surface tension using the bubble pressure method and found there was some difference in wetting with surface ages ranging from 10 milliseconds to 10 seconds at 20 °C. However, the results were not conclusive and there was no significant correlation with the frequency of solder balling. Advanced surface chemistry involves the study of the synergy between different surfactants upon the formation of micelles in order to arrive at boosted performance at the lowest concentration.

Bubble Pressure Method:

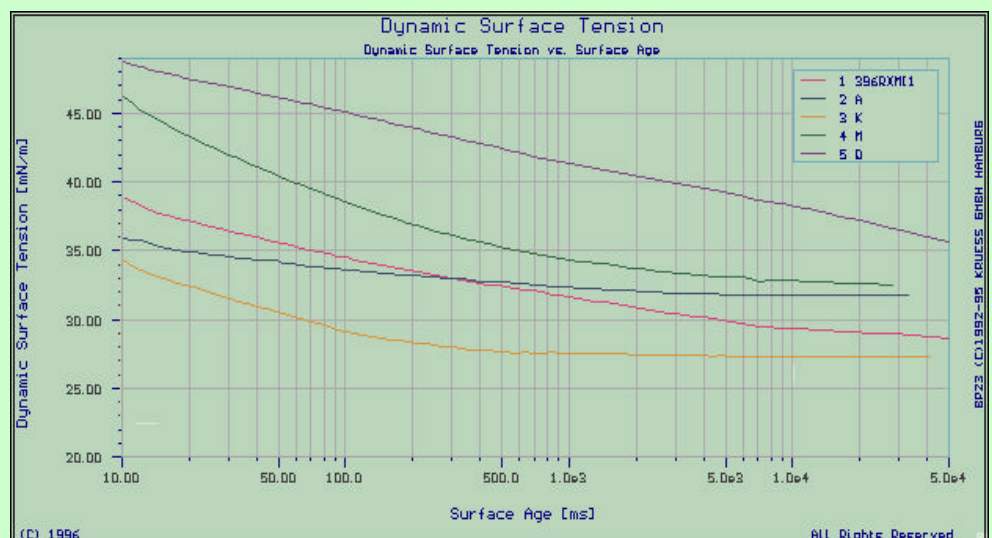
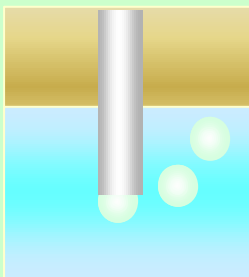


Figure 12: Dynamic Surface Tension at 20 °C of the newly developed flux compared with 4 commercially available fluxes. Distinct differences can be noticed at both short and longer surface ages. The fluxes M and Q show a higher surface tension in all areas. Product A starts lower than the newly developed product but ends higher. K shows the lowest surface tension at 20 °C. In the solder ball study this flux however showed a higher number of solder balls than the newly developed flux and product A.

Soldering is a process that most of all is characterized by heat, as the temperature of the flux and the circuit board rises the surface tension of the flux changes. Some surfactants react more drastically to temperature changes than others. Some surfactants even break down before the entire solder process is completed. Therefore it was interesting to study the surface tension of the flux at elevated temperature. We set the instrument at 70 °C in order to get an idea of what happens in the pre-heat phase.

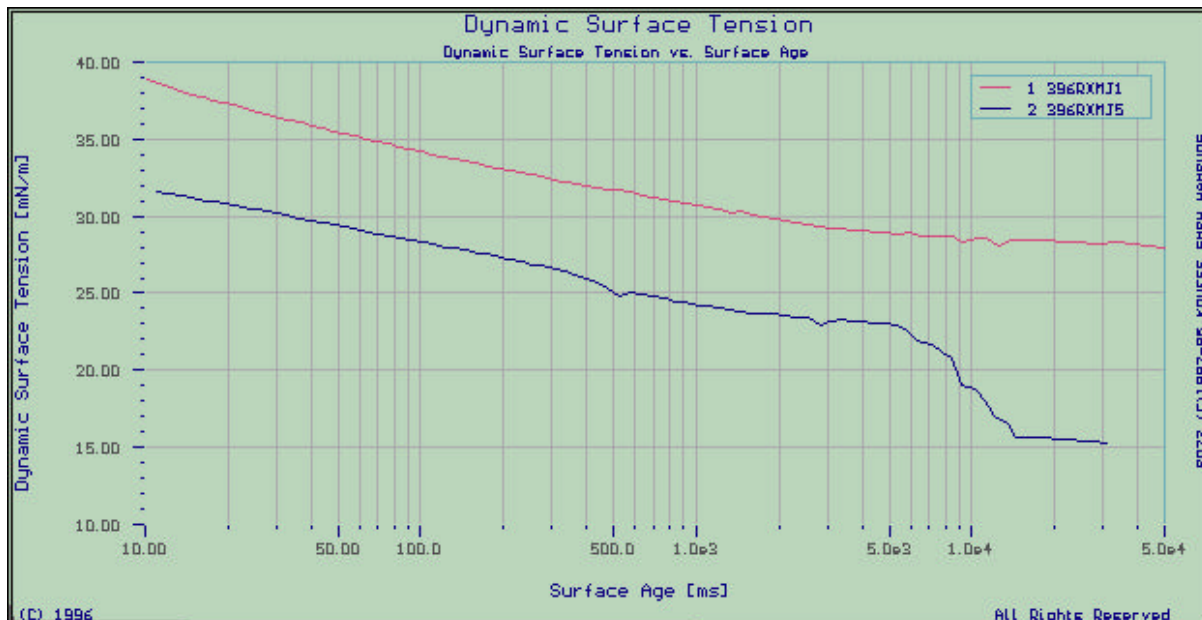
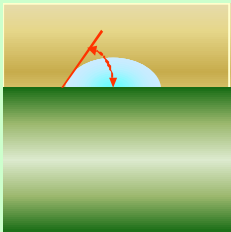


Figure 13: Dynamic Surface Tension at 70 °C and 20 °C of the newly developed flux. Note the drop in surface tension as surface age increases.

Based on Bell & Zajitschek’s work our thesis mentioned the contact angle measurement of fluxes by the sessile drop method on a substrate with a constant surface morphology as the most likely way to provide a correlation with the frequency of solder balling.



Sessile Drop Method:
This optical contact angle method is used to estimate wetting properties of a localized region on a solid surface. Angle between the baseline of the drop and the tangent at the drop boundary is measured.

Interfacial Surface Tension Contact Angle

	A
396-RXM	20,60
A	22,30
M	28,10
K	24,70

A = liquid resist

Figure 14: The measurement of the contact angle (interfacial surface tension) at 20 °C using the Sessile Drop Method. The results definitely show some correlation with the results of the solder ball count.

With the results of these experimentations we had the information needed to proceed with the leading prototype to the next logical phase of testing.

In order to optimize the physical and dielectric properties of VOC-free flux residues we used two different strategies. First of all we pruned back the surface-active materials by using the concept of the critical concentration. Consequently we verified the performance with regard to

solder balls. Beside the surface-active materials VOC-free fluxes may consist of multiple polymer species and property modifying additives. The additives affect the mobility of the system, water retention properties, long and short term dielectric properties and thermal behavior.

Using thermogravimetric analysis and differential scanning calorimetry, we have characterized the crystallization behavior, sublimation energy and optimum activity range of several organic acid systems suitable for use as flux activators. With this information it is possible to tailor the activator for the thermal envelope required to volatilize the water-based vehicle in VOC-free fluxes. Properly applied, these techniques can allow substantive decreases in residue mass while still maintaining adequate levels of surface activation.

The results of these studies can also be correlated to surface insulation tests. Using these techniques, we have modified the residue morphology to increase both initial and long-term surface insulation resistance, resulting in a system with vastly superior surface insulation resistance properties. We subcontracted the reliability testing of the final version of the new Cobar product, 396-RXM according to the IPC-J-Std-004 standard, to an internationally accepted, independent laboratory. The results are listed in table 8.

IPC/ANSI-J-STD-004	
SIR	Pass
Corrosion	Pass
Copper Mirror	Pass
Fluoride Spot Test	Pass
Halides	none
Non-volatile Matter	2,3% w/w

*Tested by an independent Laboratory.
Reports available on request.*

Table 5: The flux was sent to an independent, internationally known laboratory for qualification testing according to the IPC-standard. The report may save time and money for those users who wish to verify the integrity of the flux.

The use of DSC and TGA techniques have also helped us boost the performance in soldering results. We verified this by dynamic soldering tests on the so-called new surfaces such as OSP and Nickel/Gold.

The different interfaces with solder resists

We believe that the correlation between solder balling and the chemistry of solder fluxes can be explained with the concept of surface tension. For our explanation we need to consider that Bell & Zajitschek have observed two important phenomena.

First they found a correlation between the differences in element concentration in the solder resist and the tendency for solder balling. The solder resist with a higher oxygen content most likely need a selective collector adsorption into the resist surface so it can hydrophobize the surface in order to prevent wetting of the solder resist by the molten solder.

Secondly Bell & Zajitschek established that variations in the ionic contamination of the bare boards - as an indication of process tolerances in the board manufacturing operation - significantly influence the tendency for solder balling. To address this phenomenon surfactants in the flux are partially adsorbed onto the surface of the contaminants or embedded in the surface of the solder resist.

The presence of the surfactants promotes the dissolution of the contaminants. Depending on the process history of the bare board possibly varying amounts of soluble contaminants is present just below the surface of the solder resist. They dissolve into the flux to increase the ionic strength of the flux and salt out additional molecules of surface-active species at the interface. Additions of salt to the surfactant solution are known to lower further the surface tension of a system, but not at all surface ages! Also, the accumulation of salt in a flux increases the tendency for the formation of micelles. By consequence one can assume that free, unassociated surfactant molecules are preferred for the lowering of the surface tension of fluxes. In previous investigations with high-speed photography in a wave-solder experiment with glass plates coated with solder resist, but not fluxed, we have observed gas

bubbles between the circuit board and the molten solder. Depending on the type of solder resist the bubble formation showed significant differences. As no flux had been applied and the samples had been carefully prepared prior to the experiment, we assume that the outgassing of chemical species from the solder resist caused the bubbles.

We recently repeated this experiment. This time however, we applied different VOC-free fluxes to the surface of the coated glass-plates. Observations clearly showed that the surface-active materials in the solder flux influence the size of the gas bubbles.

Also a correlation between the flux-chemistry that minimized the gas-bubbles and the tendency to eliminate was noted.

Conclusion

This study showed that surface tension of a solder flux at 20 °C, neither under dynamic conditions nor in an equilibrium state, does predict the probability of solder balling. Dynamic surface tension measurements are a useful tool in the development of solder flux with powerful blends of surface-active materials at the lowest possible concentrations. Contact angle measurements between fluxes and several board surfaces seem to be able to provide useful information to establish a correlation with solder balling. More work needs to be done to confirm these thesis. The present VOC-free flux technology, as developed by this program, presents a strong key to the prevention of solder balling. Fluxes now seem to have more weight as a parameter in this context than 4-5 years ago when Bell & Zajitschek investigated their contribution.

The twist that makes the newly developed product different than the commercially available products is the carefully designed and tuned activator and surface active material that ultimately provides assemblies free of solder balls and residues.

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