Performing Flux-Technology for Pb-Free SN100C Solders

Ineke van Tiggelen-Aarden, Technical Director and
Eli Westerlaken, CEO, Cobar Europe BV

SN100C (Sn99Cu0.7 with Ni- and Ge-micro-additions) is a lead-free solder alloy that is finding increased acceptance globally and holds promise as a mainstream solution in terms of long-term solder joint integrity when compared to SAC-alloys. This material has also been reported to offer superior characteristics to SAC-alloys in terms of reduced Cu erosion of assemblies, better fluidity and drainage in wave and selective soldering, and superior wettability.

However, like virtually all lead-free solders, the solder melts at a higher temperature than lead-based solders and therefore drives the industry toward thermal profiles that are considerably more demanding to all of the materials comprising the circuit assembly, including the wave soldering flux.

As temperatures rise, the flux materials undergo changes in their physical and chemical properties such as the evaporation of volatile fractions, their surface activity, and their melt viscosity. The consequence for the solder flux is early displacement by the scrubbing action of the solder wave, and ultimately the thermal breakdown of the material. This results in loss of its functionality as a protective blanket, and the loss of an insulating film over the liquid solder when it wicks up the barrel of the via or through-hole. The latter result, in conjunction with the larger Δ-T in Pb-free processes between the bottom and the top side of the printed circuit assembly passing through the solder wave, results in early solidification before the liquid solder is able to wick up the barrel and wet the top side of the pad. This defect is commonly referred to as ‘inferior topside wicking.’

Whereas the use of a N_2 blanket over the solder wave prevents oxidation and thereby assists the wetting and wicking, it does not impact the melt viscosity, and thus the displacement, of the organic materials in the solder wave.

Unlike ordinary rosins, modern fluxes may consist of multiple polymer species and property modifying additives. The additives affect the mobility of the system, solvent retention properties, long and short term dielectric properties, and thermal behavior. The key to maintaining all desired product attributes as well as maximizing topside fillet performance lies in a thorough understanding of the interactions between these polymers and certain properties of the modifying additives.

This paper describes the development and implementation of state-of-the art fluxes in the categories alcohol-based, low-VOC, and VOC-free technology, for use in Pb-free and N_2-free, SN100C-based wave soldering processes. It explains the need for flux systems that incorporate organic materials of a more advanced molecular structure. Additionally, the chemical functionalities for enhancing the mobility of these materials, impacting topside fillet performance has been studied using methods including Thermogravimetric analysis and differential scanning calorimetry. Melt viscosity, sublimation energy, optimum activity range, weight loss, and phenomena such as surface energy of a number of organic materials suitable for use in Pb-free wave solder fluxes have been characterized.

With this information, it is possible to tailor the organic system for a specific thermal profile and dramatically accelerate the wetting of the metallic regions of the circuit assembly. Properly applied, these techniques may allow substantive increases in wicking performance mass while still maintaining all other desired product attributes.

The Thermal Profile for wave solder processes with SN100C

Field experience in recent years has shown that the thermal profile for this material’s wave solder processes is similar to those based on SAC-alloys with a topside temperature of the circuit assembly prior to entering the solder wave at 110-120^{o}C (230-248^{o}F) and a wave solder temperature of 260^{o}C (500^{o}F).

As with all other alloys with a higher solidus/liquidus temperature, special attention needs to be given to meeting the specifications of topside fillets, as it is quite often observed that solder does not fully wick up and onto the pads of the topside of the assembly when soldering with these higher melting point alloys.
Whereas some roots for this phenomenon may be found in the difference in wetting, when compared to the wetting properties of Pb-based solders, the main root cause lies in the difference in thermodynamics and related parameters when the solder has to wick up the barrel of the through-hole.

When soldering with the present state-of-the-art wave soldering equipment, the heat required to successfully solder the circuit assembly in the solder wave comes through the contact with the liquid solder touching the bottom side of the circuit assembly. There is no heat source on the topside of the assembly providing an equivalent thermal energy.
By implication, there is a ΔT between the bottom and the topside in the barrel of the through-hole.

A second assumption can be made that the higher the solidus temperature of the alloy, the more critical the ΔT between the bottom and the topside in the barrel of the through-hole becomes.

This can easily be understood when considering the fact that the solder from the surface of the wave generally already begins the wicking process at its set temperature. Because of the wicking, and the heat exchange with the different mass in the barrel, the temperature of the solder decreases significantly. Because of the ΔT between the bottom and the topside in the barrel, this decrease is accelerated as the solder rises up in the barrel. When the solder temperature decreases, a number of thermal properties are affected, including melt viscosity, surface tension and wetting and diffusion performance.

Whereas the first remedial attempt would be to develop a flux with a substantial thermal bulk to act as a thermal blanket floating on the rising solder in the barrel, thus inhibiting the required thermal properties of the solder, the conflicting requirement that No-Clean soldering technology by its nature requires the absolute minimization of the non-volatile material in the flux is of imminent concern. One could make an analogy between a race car with a strictly controlled weight limit and a No-Clean soldering system. The way to make performance improvements in the race car is not to design bigger and bigger engines, but rather to tune an engine of optimum size as carefully and precisely as possibly and boost performance by technical skill rather than brute force. In the soldering flux, of course, we can no longer put another shovelful of activator into the tank; instead, we must carefully and accurately characterize the behavior of the fluxing system as it travels along a known thermal history. We can eliminate the "chemical deadwood" and prune back constituents that provide excessive activation at inappropriate points on the time line.

The first step in any investigation of the thermal history of a No-Clean solder fluxing system is to gather data on typical thermal histories of commercial soldering processes. For this purpose, we use benchmark profiles which have been projected from production floor wave solder equipment operating with the new solder and programmed in our TGA/DSC instrument.

This instrument consists of a sample holder comprising thermocouples, sample cups and a ceramic or metallic block; a furnace; a temperature programmer; and a recording system. The key feature is the existence of two thermocouples connected to a voltmeter. One is placed in an inert reference material such as Al_2O_3, while the other is placed in the test sample material. As the temperature increases, there will be a brief deflection of the voltmeter when the test sample is going through a phase transition. This occurs because the input of heat will raise the temperature of the inert substance, but be incorporated as latent heat in the material changing phase. The instrument has ample capacity to exactly simulate any thermal profile in a Pb-Free soldering or reflow process.

With the differential thermal analysis the test sample and an inert reference sample are heated (or cooled) under identical conditions, while recording any temperature difference between test sample and reference sample. The instrument offers a choice between a time or temperature plot of the differential temperature. Changes in the test sample, either exothermic or endothermic, can be detected relative to the inert reference sample. Thus, a DTA curve provides data on the transformations that occurr, such as glass transisition, melting, boiling, sublimation and recrystallization.

A DTA curve can be used for fingerprinting (identification) of single raw materials or of blended products.
The same instrument quite often also can be used to determine integral weight loss of materials when going through a preprogrammed temperature profile.

Before formulating prototypes, we characterized the individual raw materials in each functional group of a wave solder flux with the benchmark profile in the TGA/DSC instrument in our labs in Breda, Holland.

For the sake of the discussion we hereby provide a breakdown of a solder flux formula into its functional groups for the categories Alcohol based, Voc-Free and Low VOC fluxes.

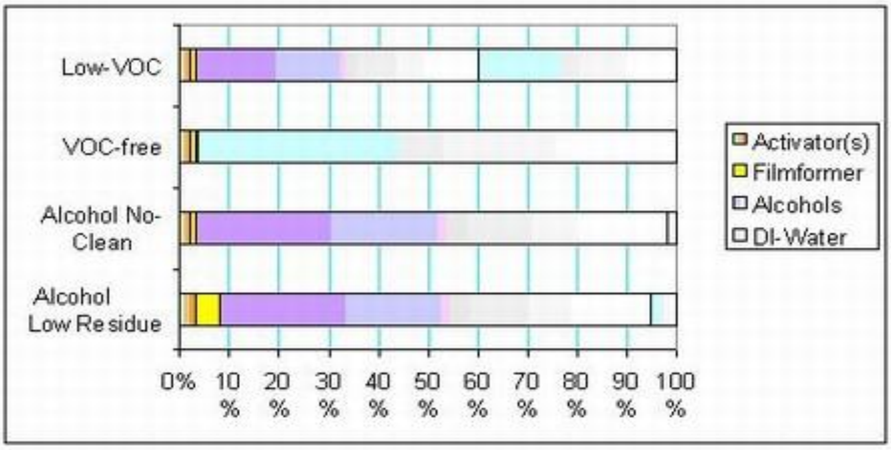

Figure 1: A global breakdown of flux compositions into functional groups in approximate ratios [% w/w].

For the purpose of providing a thermal insulating blanket, film formers are an important functional group in a wave solder flux.

Their thermal properties are not only limited to the support that they can provide to wetting action by the activator system, but also their thermal bulk and – last but not least – their melt viscosity. Other functions include their contribution to the surface tension, their potential to neutralize post-solder ionic residues, etc.
Figure 2 shows some film former materials of different chemical nature:

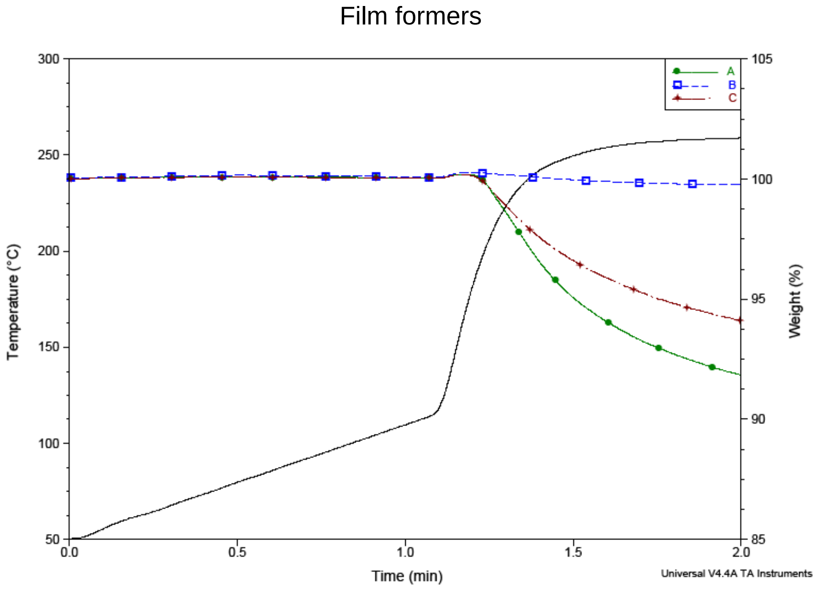

Figure 2: Some materials with film-forming functionality compared in an TGA-curve, simulating a benchmark wave solder profile for the new solder.

Material A is a hydrogenated, esterified resin with a certain melt viscosity and hydroxyl content. Its stability at elevated temperatures is the lowest of the three materials in this group. Material B is a material of a different chemical family with a molecular structure 100 times larger than material A. It is a material of relatively limited mobility, yet it has some specific film forming features.

Plasticizers can play an important role in the uniform distribution of the other functional materials in the wave solder flux, in particular the film formers. In order to make sure that they continue to perform toward the end of the soldering process, they need to survive the heat excursion of the Pb-Free process.

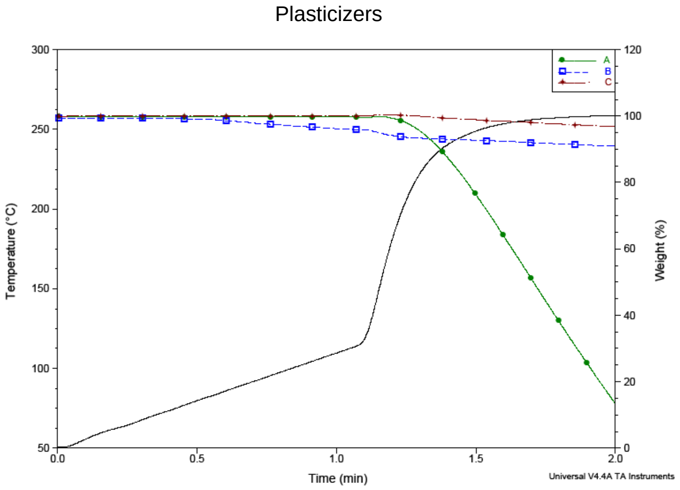

Figure. 3: Some materials with plasticizer functionality compared in an TGA-curve, simulating a benchmark wave solder profile for the new solder. Material B, the blue curve also has a very specific melt viscosity.

Figure 3 shows some plasticizer materials of different chemical natures.
Material A is a complex non-toxic ester. This substance shows a dramatic breakdown when the temperature reaches 200^{o}C. Material B is a non toxic ester as well. The weight loss stability is superior over material A, yet material B has a unique melt viscosity profile, making this material the preferred choice to any formulator who strives for minimizing and the most uniform spread of post solder residue by the scrubbing action of the solder wave. Raw material C can be qualified as a slight irritant when compared to the other plasticizers. In general, health concerns have resulted in a negative reputation of many plasticizers.

We have characterized many common flux activator systems with the same type of instrument used in previous studies, the Differential Scanning Calorimetry (DSC) analysis. By observing the difference in heat flow between the sample and reference, the DSC-analysis is able to measure the amount of heat absorbed or released during such transitions.

Reading from a DSC-curve, it is important also to note the very sharp melting range of adipic acid, a very typical No-Clean flux activator. Organic acids, unlike halide salts are only weakly ionic in solvent solution. Their metal cleaning "horsepower" is very much increased when they enter the more mobile liquid melt phase. There is, therefore, a rough correlation between melt range and cleaning efficiency. While the sharpness of the melt range in a DSC-curve is an excellent indicator of the purity of the starting material (an essential parameter in No-Clean fluxes) the position of the peak is important because it gives a "quasi empirical" indication of the temperature range at which the activator "kicks in". In Figureure 4 one can observe the overlay of different scans of adipic acid modified by the addition of several synergistic dicarboxylic acids and certain proprietary non-halide, non-acid materials. It is readily apparent that the melt peak has been substantially broadened, and that some additional peaks at the lower temperatures have been added. The melt temperature of Adipic acid has also been lowered by almost 10 degrees indicating a much earlier availability of the soldering power of this major constituent. The lower temperature peaks assist in initial cleaning of the substrate and initiate the fluxing reaction. For the survival of the bulk of the activator towards the end of the reflow profile it is quite important to characterize the integral weight loss of the material concerned.

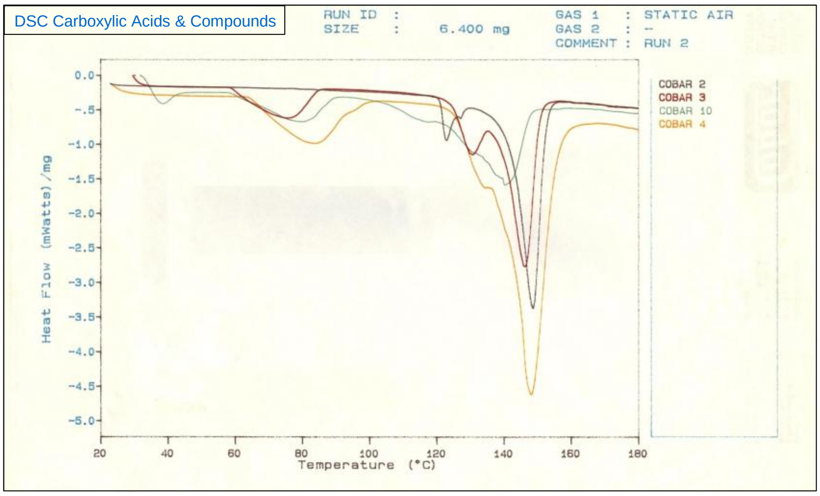

Figure 4: The DSC-curve for 4 different di-carboxylic acid based activator systems. The various modifications have resulted in boosting the enthalpy in some of the peaks and shifting, adding and broadening of the peaks.

By experience and observation we have seen that some activators are better than other in certain applications, but there is not single activator that is universally better than all others in all applications and in all soldering systems[3].

However, it is always a valid statement that the cleaner and the more "solderable" a surface one has, the less activator is necessary to solder it. If we can continuously optimize the cleaning of the metal surface at lower temperatures with organic materials that are highly volatile and have the proper resolidification behavior, the surface will become substantially more solderable. When the final organic acid "kicks in" the cleaner surface will result in less need for that final "difficult to completely volatilize" activator material in order to obtain good soldering performance.

Figureure 5 shows an interesting comparison between the weight loss results of the original adipic acid and its smaller brother in the di-carboxylic acid range, succinic acid and compound with each of these acids.

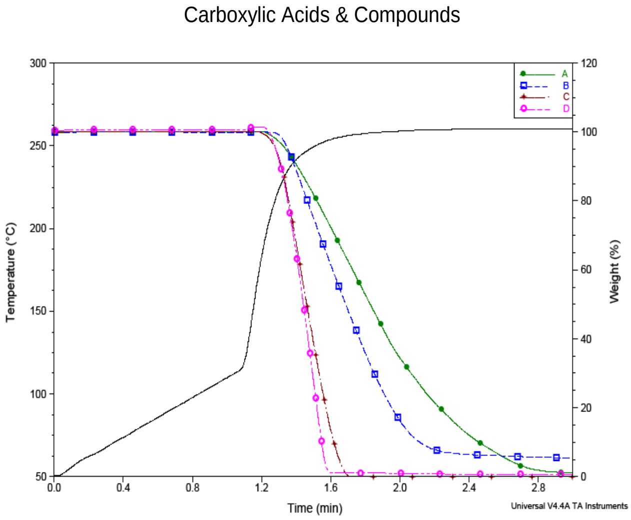

Figure 5: Some di-carboxylic activators compared in a TGA-curve, simulating a benchmark wave solder profile for the solder.

Material S is adipic acid, pharmaceutical grade. This substance shows a slightly earlier initial weight loss than the compounded adipic acid, material B. The later material experiences a much shaper decline in weight than the original adipic acid. At the end of the curve, however, the compounded material shows a somewhat higher thermal stability again.
A similar mechanism can be observed with succinic acid, material C, and its compound, material D, with the exception that the weight loss at the end of the curve for both materials is the same.

Material A represents adipic acid. The pharmaceutical grade of this activator has a harp melt point at 151.9°C at normal atmospheric pressure. Weight loss begins at a temperature of 215°C and proceeds rapidly at solder wave temperatures until all but the thermal breakdown products remain. This occurs at temperatures just slightly beyond those used for normal wave soldering. By compounding adipic acid or by blending this material with other surface active materials, the DSC-peaks of a compound or multi-component system can be broadened and/or added with several smaller lower temperature peaks. Also, the weight loss of the original acid can be shifted a substantial number of degrees C and weight loss begins at a proportionally higher temperature. The implications for the soldering process of these very subtle changes are enormous. It graphically demonstrates that simple systems, such as adipic acid, are not capable of sustaining themselves through the wave soldering process. They do exactly what we desire them to do; they break down and lose some of their bulk cleaning power. But they do it just when we need them most...just prior to joint formation.

Using the data from our differential scanning calorimeter, we were able to modify our activator and synergist system to remove the constituents that caused the anomaly and replace them with other more effective systems. Further, the ultimate system displays exceptional soldering ability as well as strict compliance to SIR and electro-migration criteria of most common international standards in this respect.

Surface Chemistry

Now, we must also remember that successful wave soldering of P.C. assemblies requires not only perfect wetting of metallic surfaces and wicking up the barrel of through-holes, but perfect de-wetting of non-metallic surfaces as well.
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 consideration.

This is the true role of our understanding of interfacial chemistry. Not only is it necessary to deliver the activator systems smoothly and reliably to the metallic surfaces, but it is also important to ensure that the molten solder mass smoothly, reliably, and completely separates from the non-metallic when the board exits the wave. During the pc-board fabrication process, the resist absorbs bits and pieces of everything it comes in contact with and during the soldering process begins to volatilize most of that material. The solder flux therefore must exhibit both a detergency and a highly-controlled surface energy during the time that it is in contact with the solder wave. It must rapidly spread over the entire surface, displace the contaminants, and build a uniform monomolecular film which presents 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 acidic environment of the solder flux.

Surface tension considerations alone are not enough to give us a complete understanding of this phenomenon. Surface energies are also very important.

Overall Surface Tension & Capillary Viscosity			
Flux type	H_2O % w/w	ST [mN/m]	mPa.S
Alcohol based fluxes			
1	5	22,6	2,976
2	2	24,2	3,001
Low VOC fluxes			
3	22	23,6	2,761
4	40	25,8	2,305
VOC-Free fluxes			
5	94	30,2	0,942
6	97	29,2	0,922

Figure 6: SurfaceTension & Capillary Viscosity data measured respectively with a Wilhelmy plate @ 20°C and a Grabner Minivis @ 25°C with microball, on overall flux formula do not discriminate between mediocre and well performing fluxes for the solders

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 conFigureuration during the very high temperature excursion through the solder wave. This implies a strong charge binding mechanism, at least during that phase of the soldering process.

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 control both the surface tension and the interfacial tension at the solid-liquid interface.

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

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.

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.

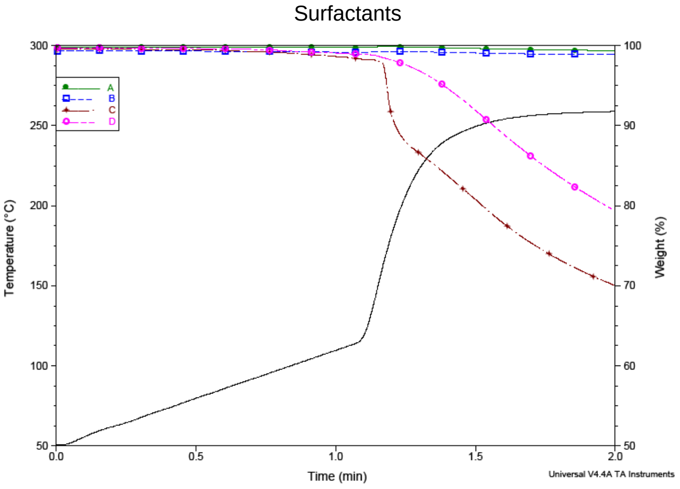

Figure 7: The thermal stability of surfactants at elevated temperatures is equally important to the tuning of the blend of surfactants different categories

A properly designed surfactant system will not only assist the wicking of the solder flux up the barrel of a through-hole, it will also assist in the repellence 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; this is essential for controlled distribution of the flux and sufficient capillary activity in vias and through-holes. Surfactants will reduce the bubble size of gases 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, indeed in many cases eliminate, problems of solder balling, and will aid uniform heat transfer during the wave solder process. It has become obvious that surface chemistry in advanced No-Clean solder fluxes has developed far beyond the requirement of a "foam additive".

High ratios of surfactants would create more ‘cons’ than ‘pros’:
- more residue
- uncontrolled foaming properties
- uncontrolled spray applications
- reduced SIR values
- increased costs

Finally, 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. Chemical and thermal stability are keywords in this context.

The overall TGA curve of products is very much influenced by the bulk of their solvent systems as shown in Figureure 8a. Evidently, the VOC-free system, primarily based on DI-water, requires more energy to evaporate and evaporation of the bulk of the water occurs later and at higher temperatures than alcohol-based products (Figureure 8b). It can also be understood from the curves in Figureure 8a that fluxes from the low-VOC category can be considered a drop-in replacement for alcohol-based fluxes when concerning heating profile requirements

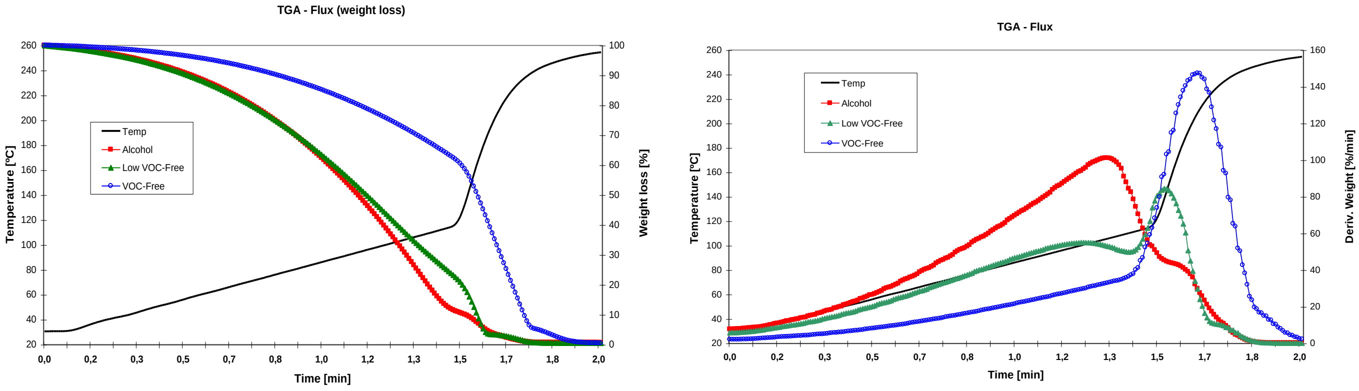

Figure 8a, Left, showing the integral weight loss solder fluxes showing excellent solder result with perfect topside wicking with SN100C solder. Fig; 8b, Right, shows the weight loss per time-unit when the temperature rises.

Melt viscosity

The wash-off effect of the solid materials by the solder wave as well the wicking is influenced by the melt viscosity of the solid materials in the solder flux. Fluxes including solid materials with a distinct melt viscosity have shown better performance in both the spread of the residue, the cosmetic as well as the ionic cleanliness of the post solder assembly surface but also in the topside wicking performance.

With plate/plate rheometry in oscillation mode[1] we increased the temperature in a continuous ramp from 20 to 110^{o}C while setting the oscillation to a constant frequency of 1Hz and an amplitude of 2.5’. In this mode we measured the flow behavior of the individual raw materials through their complex viscosity[2]. In Figureure 9 some of the results have been brought together. Raw materials A and B are plasticizers of a different chemical nature. Please, note the superior stability of material A at temperatures beyond 50^{o}C. Material A follows a distinct with a sharp drop in viscosity which is initiated as soon as the temperature goes up. At 90^{o}C and beyond, the viscosity is practically 0 mPa*S. The surface active materials C and D also show a significant difference in their flow behavior in the application phase. Material C will stay on the spot to a certain extent when the pressure of the solder wave attempts to displace the flux.

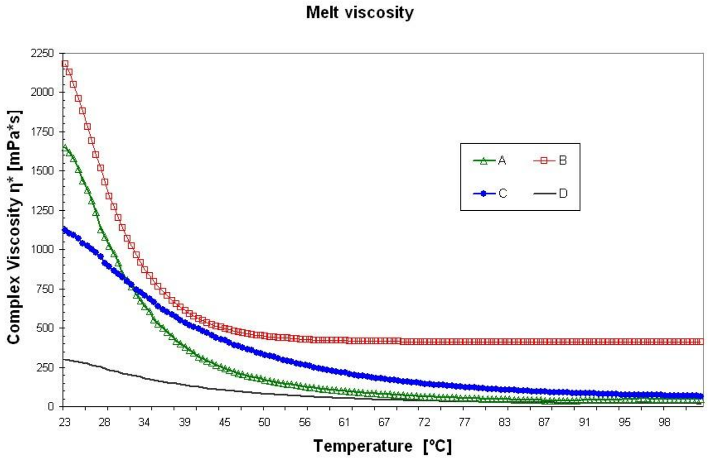

Figure 9: The melt viscosity of some raw materials in different categories determined by oscillation rheometry while heating samples in a continuous ramp from 23 to 100^{o}C

Conclusion

Due to the impact of the bulk solvent system for performing wave solder fluxes for the new solder in different categories, none of the individual analyses techniques such as TGA/DSC, Surface Tension and viscosity, nor a combination of these techniques, is capable of characterizing the performance products compatible with the SN100C wave solder process. Only analyses of the individual raw materials and blends of the solids can provide information to the formulator that he can use to develop better performing solder fluxes. Compounded materials showing their thermal stability by means of their TGA/DSC results in conjunction with specific melt viscosities and, in the case of surfactants, in conjunction with the ability to address specific solids/liquids and liquid/liquid interfaces, are the basis of performing flux technology for the new solder.

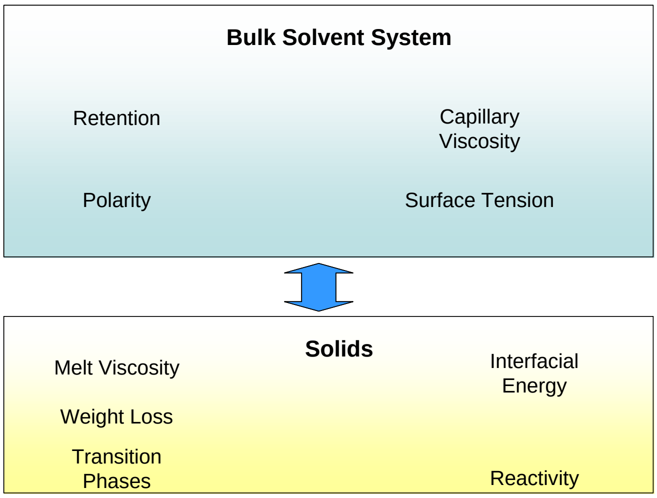

Figure 10: A simplified model mapping the parameters in a solder flux that determine its wicking performance in new solder processes.

Figure 10 illustrates a simplified map of parameters of the individual raw materials, finally defining the wicking performance of solder fluxes in the new solder processes. Evidently, there are interactions between some of the parameters in the model. Based on dynamic surface tension determinations of fluxes at elevated temperatures, we know that the solvent retention has a significant impact on the surface activity of the solder flux. Some of these interactions require further study. Our conclusion is that the flux formulator indeed can develop performing products for the new solder process. However, solid knowledge of the relevant thermal properties of the raw materials is a prerequisite.

Sources

1 A Fast, Precise and Reproducible QC-Rheometry Routine for Solder Paste, Ineke van Tiggelen-Aarden, Proceedings APEX-2004 Conference

2 The Complex Viscosity is determined by sinusoidal shear loads through oscillatory testing and therefore noted with an asterisk to indicate the complex form, and thus distinguish it from a viscosity value that has been established by rotational testing.