

## Hazard Assessment of High Speed Rubber Dissolution in Toluene Using Computer Modelling of Electric Fields and Potentials

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For more than 20 years published guidance on control of electrostatic hazards has advised that suitable control measures for restricting charge generation in stirring or agitating operations include: limiting the mixer power (with less than  $0.37 \text{ kW.m}^{-3}$  cited); avoiding a second immiscible phase, and; using a high conductivity ( $>10^4 \text{ pS.m}^{-1}$ ) continuous phase. Furthermore, there is much evidence indicating that deviating from these guidelines can lead to visible discharges across the surface of liquids in mixer vessels, often resulting in fires or explosions.

Preparing a suspension of solid particles in a medium conductivity liquid rubber solution using a high speed agitator (up to  $9.7 \text{ kW.m}^{-3}$ ) in the presence of a flammable atmosphere would therefore not be recommended. Indeed, the usual advice when faced with such a proposal would be to either change the process, change the materials or inert the vessel headspace to remove the flammable atmosphere.

ITAC Limited, a leading UK manufacturer of solvent based adhesives and coatings, operates a process exactly like this and having a comprehensive understanding of the electrostatic hazards associated with this operation is fundamental to process safety.

The latest international guidance on control of static hazards advises that: "Computer modelling of potential and electrical field distribution ... may be very helpful in risk assessments when handling liquids or powders", although no particular guidance is offered. Nevertheless, this paper describes in some detail the use of this approach as a means of hazard assessment for the specific situation at ITAC and represents a substantial contribution to the ATEX/DSEAR hazard and risk assessment for the company's facilities and operations.

The approach offers significant benefits in ensuring that the most appropriate and cost effective hazard control measures can be adopted in order to manage electrostatic hazards. Clearly this is a crucial part of ensuring operations are performed in a manner which protects the health and safety of staff and also maintains security of supply for the company's customers.

The paper describes how, through a series of theoretical and experimental validation trials, confidence in the modelling software was gained. Ultimately, though, the purpose is to show how a combination of experimental measurements and computer modelling was used to confidently conclude that an incendive discharge in a full scale high speed blender could be considered so unlikely that, provided all other potential ignition sources had also been appropriately addressed, inerting or other protective measures would not be required.

**Keywords:** electrostatic, static, hazards, discharges, mixing, blending, computer, modelling, fire, explosion.

### Introduction

ITAC Ltd operates a compounding facility in Radcliffe, Manchester, where they manufacture solvent-based adhesives, coatings and sealant materials. This is a well-established sector. Indeed, ITAC is a business which dates back to the early 1900s when India rubber was dissolved in petroleum solvent for the pneumatic tyre manufacturing industry. Nevertheless, it is still able to benefit from state of the art analyses and techniques such as those presented here. Adhesives, coatings and sealants can be based on solutions of natural polymers and synthetic materials including acrylic, butyl, polysulfide, polyurethane, silicones, silane modified polymers, and even reactive systems. And they are used in a wide range of applications such as roofing, construction, flooring, and encapsulation, with products being found in sectors ranging from textiles to the food industry. However, a common factor linking many of these products is the nature of the solvents: flammable and electrically insulating.

Current international guidance on control of electrostatic hazards [PD CLC/TR 60079-32-1, 2015], like its predecessors of more than 20 years, advises that where flammable atmospheres may be present some blending and mixing operations can lead to excess electrostatic charge generation and, as a result, a significant ignition hazard. Factors known to exacerbate the hazard include: continuous phase conductivity less than  $10^4 \text{ pS.m}^{-1}$ , a second immiscible phase (including solute prior to dissolution), high viscosity and high agitator power ( $>0.37 \text{ kW.m}^{-3}$  has been cited [BS 5958-1, 1991]).

On the face of it, therefore, preparing a suspension of solid particles in a medium conductivity liquid rubber solution using a high speed agitator (up to  $9.7 \text{ kW.m}^{-3}$ ) in the presence of a flammable atmosphere could not be recommended. Indeed, the usual advice would be to either change the process, change the materials or inert the vessel headspace to remove the flammable atmosphere.

However, PD CLC/TR 60079-32-1 advises that: "Computer modelling of potential and electrical field distribution based on the measurement of resistances, charge to mass and/or space charge densities may be very helpful in risk assessments when handling liquids or powders". Although no further details or guidance are offered in published guidelines and standards, DEKRA Insight (Chilworth Technology) has been pioneering combining this approach with experimental measurements to demonstrate specific processes represent only a low electrostatic ignition hazard despite generic guidance to the contrary.

The work described here does exactly that for the ITAC process already mentioned.

## Background and Procedure

Initially it had been hoped that a computer model of the mixer in question would have shown the fields and potentials predicted from even worst case literature values for liquid charge density could not lead to incendive electrostatic discharges. Unfortunately, this was not the conclusion of this preliminary work [Azizi, 2015], which meant that, other than immediately recommending the vessel should be inerted, there was no alternative but to combine experimental work with modelling for a more detailed, process-specific assessment.

### The Process

Occasionally the process might start with a clean mixing vessel, but in the normal course of events a rubber solution in toluene heel from the previous batch is already in the bottom of the vessel. The bulk of the toluene solvent is then charged to the vessel and the heel stirred in. The required quantity of formulated rubber chippings is then manually added while stirring using a high-shear dispersion blade agitator. Full dissolution of the formulated rubber then takes place over a number of hours. A final addition of toluene is made towards the end of the process to adjust the solids content of the final product.

The precise timing of agitator speed adjustments in response to process parameters is part of the proprietary skill in the manufacture of the product. However, the timing during these trials, and the maximum and minimum agitation speeds, were certainly representative of all batches.

Once the batch has passed its quality control tests it is pumped to product containers using a pneumatically operated diaphragm pump.

### The Hazard

The computer model uses the liquid charge density to predict electric field and potential values throughout the vessel. If the electric field exceeds the breakdown strength of air ( $3 \times 10^6 \text{ V.m}^{-1}$ ) anywhere in the vessel headspace the conclusion must be that there could be an electrostatic discharge (spark-like event). This may or may not be incendive to the vapours present, depending on the source of the discharge. However, it is known that if it arises from the surface of a more or less insulating liquid, and the surface potential exceeds 25 kV, the discharge is likely to be incendive [PD CLC/TR 60079-32-1, 2015].

Hence the objective of the work here was to show that, ideally, the maximum electric field in the head space would be less than  $3 \times 10^6 \text{ V.m}^{-1}$  by an appropriate safety margin. Failing that, the next best option would be to demonstrate that the maximum potential on the liquid surface would be less than 25 kV, by an appropriate safety margin.

Given the unpredictable nature of a powerfully agitated liquid, in earlier similar work [Pavey, 2015] it had been decided to use two orders of magnitude as a safety margin for electric field and a single order of magnitude for the surface potential. In other words, the maximum acceptable predicted values for safe operation were considered to be:

- Electric field in head space  $< 3 \times 10^4 \text{ V.m}^{-1}$
- Liquid surface potential  $< 2.5 \times 10^3 \text{ V}$ .

### Trials and Modelling Objective

The objective of the experimental trials and modelling was to use the model to predict the electric field in a location where it could be measured when the liquid charge density was just high enough to achieve the maximum acceptable field in the vessel headspace. This field could then be measured experimentally with the intention of demonstrating that, in reality, the process was operating sufficiently far below known hazardous levels to be considered acceptably safe.

It was also proposed to draw samples of the liquid in the vessel as the process proceeded in order to measure the charge density directly. This value could have been fed into the model with the intention of validating it by showing agreement between the measured field and the field predicted by the model for the measured liquid charge density, as had been done previously [Pavey, 2015].

Unfortunately, it was quickly shown that the charge relaxation time of the vessel contents was such that there was no way of sampling the liquid to independently measure the charge density of the vessel contents. This meant that experimental model validation could not be included in the present work, though the previous work [Pavey, 2015] still usefully provided confidence for the model outputs in this case.

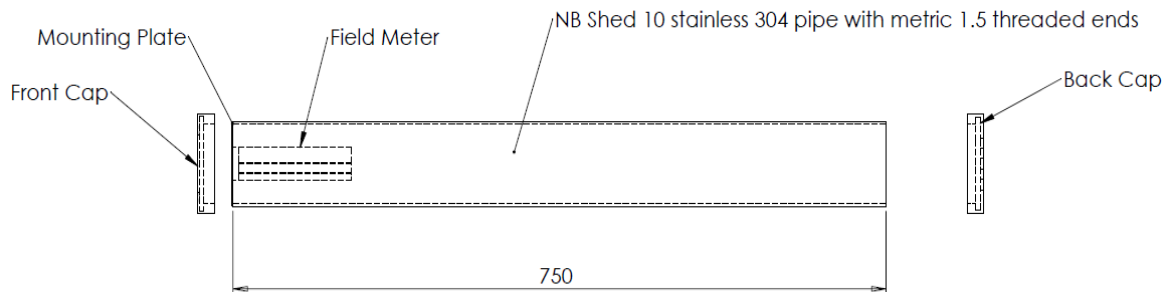
Samples were still taken to determine the conductivity and relative permittivity of the vessel contents at various stages in the process.

### Equipment

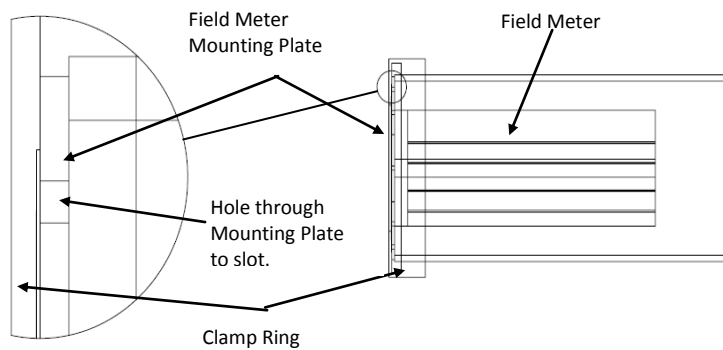
The electric field was to be measured at the inside surface of the vessel lid. There being no suitable intrinsically safe field meter for use in flammable atmospheres, a JCI 140 Static Monitor (field meter) was mounted inside a nitrogen-purged housing such that it could be safely located in the desired position. Figure 1 shows a diagram of the field meter and its purged housing. Figure 2 shows the actual unit being installed in the vessel for a measurement during the experimental trial.

The output from the field meter was logged to a laptop computer located a short distance away in a location temporarily monitored by a flammable gas and vapour detector, as required by a risk assessment for the work.

As previously indicated, periodically throughout the process, samples were taken and conductivity and relative permittivity measured. Both measurements used the same cell (as described in published guidance [BS 5958, 1991]). Conductivity was determined by measuring cell resistance with a Keithley electrometer (Model 6517A). Relative permittivity was determined by measuring cell capacitance using a Megger multimeter (Model M8035).



a) Complete Housing (detached end caps)



b) Sensor-End detail

**Figure 1: Nitrogen-Purged Field Meter Housing**

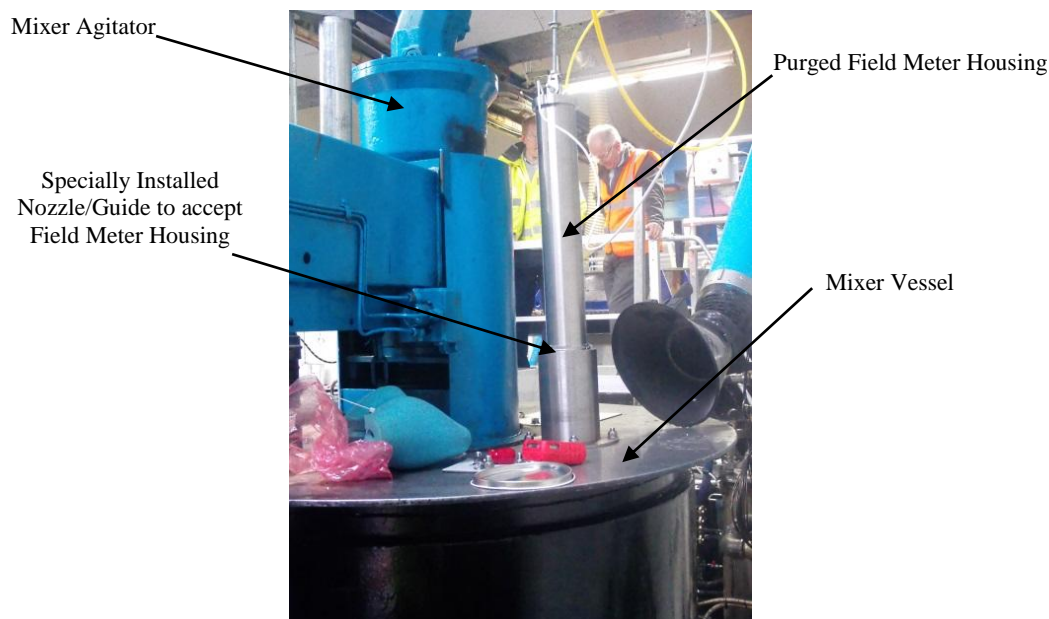


Figure 2: Field Meter in Vessel

### Procedure

Trials were undertaken during the manufacture of two batches on consecutive days. The Day 1 measurements were reported and used and supported the results of Day 2. Nevertheless, there is no doubt that during Day 1 the detailed procedures were developed and the Day 2 trial probably better represented the “normal” batch operation.

Prior to beginning, it was agreed that if the measured field exceeded certain values, either a notional “hi-alarm” or a “hi-hi-alarm” condition would be registered by those undertaking the work. In the former case measures would be taken to reduce the electric field (e.g. slowing the stirrer or stopping rubber addition), while in the latter case the run would be stopped. The “alarm level” fields were determined by the computer model as the readings expected at the field meter when the maximum acceptable field in the headspace had been reached.

To avoid the risk of splashing the field meter, it was not left in the vessel throughout the run. Instead, it was inserted into the vessel for a short period of data-logging at periodic intervals and critical moments (such as rubber addition). Later, to present these results, mean, maximum and minimum values were obtained from each relatively short period of data logging.

At the same time as logging the field, samples were taken for conductivity and relative permittivity determinations.

### Modelling

The software used for the modelling described in this paper was Sonnenhof Holdings’ LISA v 8.0.0 finite element analysis software (<http://lisafea.com>). As has been previously recorded [Pavey, 2014] this software has been validated by modelling two situations for which analytical solutions of Poisson’s equation are available [Cross, 1987]: a long earthed conducting cylinder containing uniformly distributed charge and an earthed conducting sphere containing uniformly distributed charge. The software was further validated by comparison between experimentally measured fields with those derived from a computer model, both arising from an experimentally determined liquid charge density [Pavey, 2015].

For the subsequent analysis in the present work, it was important to be able to compare the experimental field meter readings with predicted values at the field meter location when the maximum acceptable field was present in the head space. A graphical output from the model using a simplified mixing vessel (albeit still based on the full-scale dimensions provided by ITAC), with a liquid charge density chosen to just achieve the maximum acceptable internal field, is shown in Figure 3.

In Figure 3 the vessel is reasonably full so this is clearly a model output from after the rubber addition, since prior to rubber addition the liquid surface is much lower. An idealised vortex has been included in the model geometry and it can be seen from the colour coding and colour key that the highest field is at the shaft surface within the vortex. In this case, the charge density was selected to give the previously noted maximum permissible value of  $3 \times 10^4 \text{ V.m}^{-1}$ . To determine what would be seen by the field meter under this condition, it is then very straightforward to read the nodal values of field at the field meter position. In the above example of simplified vessel geometry (as seen in Figure 3) the value at the field meter is found to be

$3 \times 10^3 \text{ V.m}^{-1}$ . This then allows direct comparison between the actual measured field and the modelled maximum acceptable measured field.

However, there are further complications. The accuracy of this type of modelling depends on the way in which the volume of interest is subdivided into “elements” – the small shapes or volumes visible in the images of Figure 3. The more elements the greater the accuracy, though this is at the expense of the required computing power. In practice therefore there is normally a compromise between the available computing power and the size and number of elements.

For the present work, in every case modelled, three sizes of element were tested. Figure 3 represents the middle sized elements. By plotting a result (such as the predicted field meter reading) against element size it is possible to see that the result “converges” on a value as the element size becomes smaller. Hence, the values used to define acceptable fields in the Results section are actually these “convergence” values.

Finally, in reality there is an earthed dip pipe and earthed temperature probe in the mixing vessel. Although these would be expected to affect the fields and potentials in the vessel they do not appear in the images in Figure 3. The model used in Figure 3 was constructed by preparing a 2D projection image of half the vessel and revolving it around the agitator shaft axis to produce the 3D model. That, of course, makes inserting single asymmetric (with respect to the vessel axis) items into the model rather difficult.

To assess the necessity (or otherwise) of their inclusion, a model constructed in another way, with a flat liquid surface, was tested with and without the inlet dip pipe and temperature probe. This assessment was carried out for the liquid levels both before and after rubber addition. In this way, it was shown that the effect these items had on the field meter reading was to attenuate it, but by no more than 5%. It was therefore concluded that they did not need to appear in the main model.

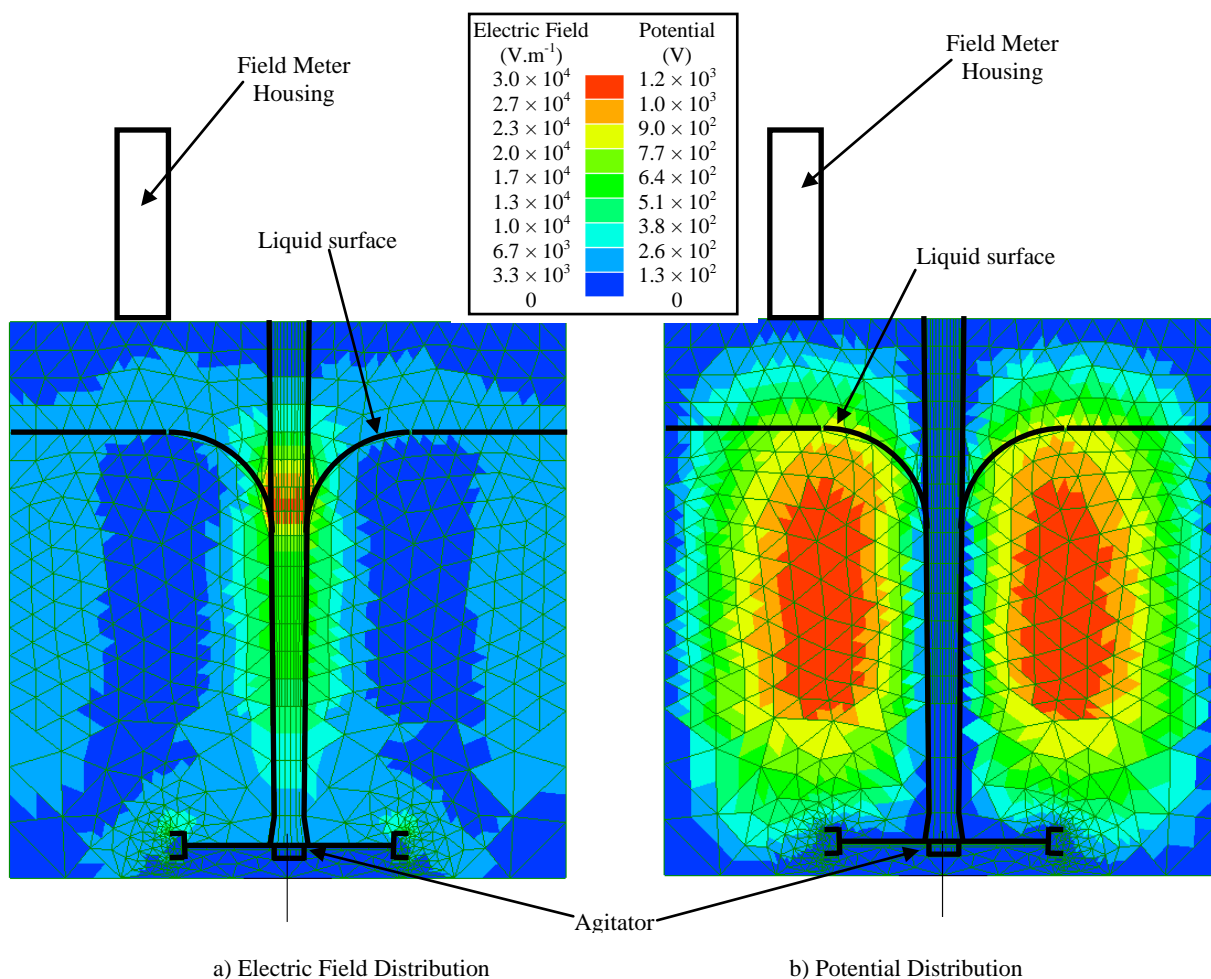


Figure 3: Typical Graphical Output from Model

## Results and Discussion

The results of the two days of trials have been incorporated into the two graphs which appear in Figures 4 and 5 below.

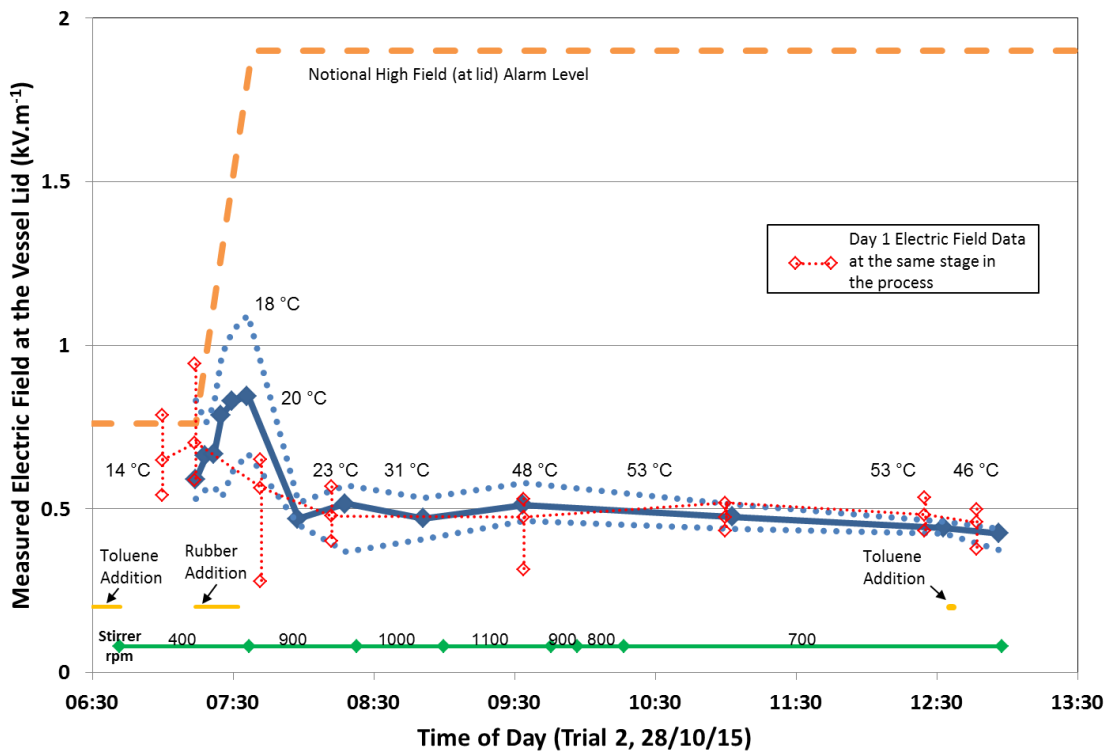


Figure 4: Electric Field Results

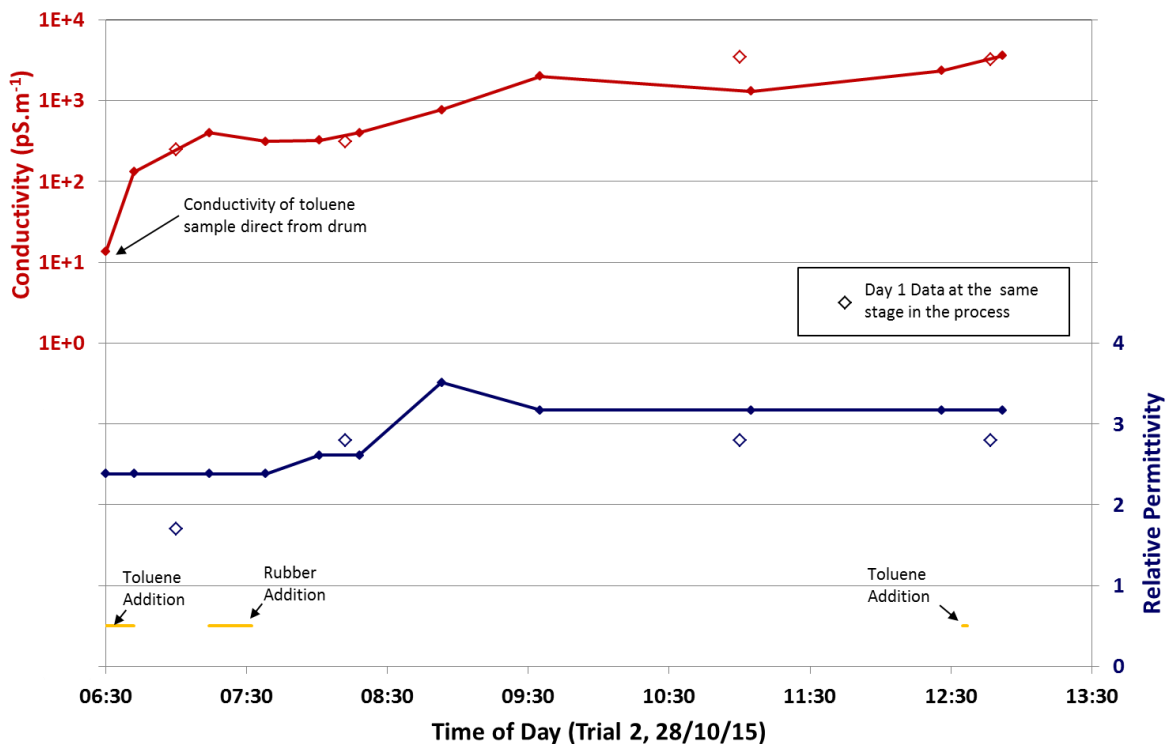


Figure 5: Materials Property Results



Figure 4 shows the average, maximum and minimum fields detected on both Day 1 (red dotted lines) and Day 2 (blue lines) during the relatively short periods when the field meter was in place. Several other items of information can also be seen in Figure 4. The field predicted at the field meter if the maximum field in the headspace exceeded the breakdown strength of air with the safety margin previously discussed applied is shown as an orange dashed line. The stirrer speed is given numerically on a horizontal solid green line towards the bottom of the graph. Material additions are shown by short yellow lines a little above the stirrer speeds. And batch temperatures are given numerically at various points along the monitored field curve.

Figure 5 uses the same time axis as Figure 4 for ease of direct comparison with the processing stages. The main data shown on Figure 5 are the conductivity of the batch (referenced against the left hand axis) and relative permittivity of the batch (referenced to the right hand axis). Material additions are also shown as on Figure 4.

In Figure 5, the first conductivity measurement is for toluene taken directly from the drum. This showed a conductivity of  $10 \text{ pS.m}^{-1}$ ; somewhat higher than the normally assumed figure for pure toluene ( $1 \text{ pS.m}^{-1}$ ) but still well below the limit of  $50 \text{ pS.m}^{-1}$  which is commonly taken as the boundary defining low conductivity (insulating) liquids [HSG140, 2015]. Interestingly, once this was added to the heel in the vessel from the previous batch, the conductivity increased by an order of magnitude. This is very significant and really indicates that a heel, or an equivalent heel taken from a previously made batch, should always be in the vessel before the first toluene addition – even if the vessel has previously been fully cleaned. It would also be appropriate to check the conductivity of the toluene plus heel at this point; just to be sure it truly is appropriately conducting. The conductivity continued to rise as the batch process proceeded, though this initial increase is certainly the most important.

In Figure 4 it can be seen that the field increased significantly as the rubber was added and even threatened to cross the “alarm” level field which has also been included on the graph. Incidentally, the alarm level increases during rubber addition because during this period the liquid level rises towards the field meter. Hence, even if the alarm field and potential at the liquid surface remain constant, the field meter mounted at lid level will see higher fields as the liquid surface approaches it.

The field levels during initial rubber addition did threaten to cross the line, though it must be remembered the only values which did cross were maxima from a period of data logging. Hence, these relatively high values may have lasted for no more than one second – the frequency of logging. Furthermore, the previously mentioned and notional “hi-hi-alarm” level at this point would be about  $2.2 \text{ kV.m}^{-1}$ , which is just off the top of the graph. Nevertheless it is recommended that nothing should be done to exacerbate charging at this stage of the process. Especially it is recommended that the stirrer speed should be kept to the lowest level practical during rubber addition.

However, once rubber dissolution is well under way, the recorded fields were found to be well below problem levels for the rest of the batch. On that basis, and with the recommendations already mentioned, it is concluded that running the observed process is unlikely to lead to an incendive electrostatic discharges provided the process and process materials are not changed in any way. Some of the formal recommendations below are aimed at ensuring that even inadvertent changes cannot slip through.

## Conclusions and Recommendations

Electric fields and electrical properties of process materials were monitored in the mixer during manufacture of two batches over two consecutive days. By combining the experimental data with computer modelling, and specifically the predicted limiting values based on the computer model of the full scale process equipment, it was possible to demonstrate that in reality the process was operated with an adequate margin of safety as far as the ignition hazard arising from unwanted static charge was concerned.

Hence, on the basis of the results reported, for the particular process being assessed it was concluded that, provided no changes were made, the risk of an ignition due to electrostatic charge generation as a result of the described high speed mixing process, could be considered acceptably low. The benefit to ITAC Limited, the company operating the process, was that safety for personnel involved with, or working near, the manufacturing process could be demonstrated without the need for inert gas blanketing of the mixing vessel or the provision of technical protection measures such as explosion venting. However, in considering why this is so, a number of formal recommendations are itemised below.

From the comments here and in the previous sections it is clear that ensuring this remains the case relies on ongoing compliance with a number of guidelines. Specifically these were itemised as:

- Process materials and the process operations should not deviate from those which were used at the time of the assessment trials. That includes, but may not be limited to, the vessel, inserts in the vessel (e.g. dip pipe, thermocouple), the agitator, agitator drive and the composition of the formulated rubber.
- If there is no alternative to changing the process, the process materials, or both (contrary to Recommendation a), the revised operation must be subject to a full assessment to ensure continued safe operation taking full account of, amongst other things, the possibility of electrostatic charge generation during processing.
- Prior to agitation and significant rubber addition the vessel contents should include a heel of around 20 litres (18 litres was indicated during the trials) from a previous completed batch mixed with the fresh toluene. This is a requirement even if the vessel has previously been fully cleaned. In that case a quantity of a previous batch equivalent to a heel must be charged to the vessel as the first step in the process.

- d. The conductivity of the heel plus toluene should be measured before rubber addition commences. The equipment and procedure given in standards [BS EN 60079-32-2, 2015] is suitable and, on the basis of the results in Figure 5, it is recommended that the conductivity should not be less than  $100 \text{ pS.m}^{-1}$ , though there will be a degree of learning, initially. This will probably pick up any significant changes to the rubber composition, even if they are not otherwise apparent.
- e. The stirrer speed during rubber addition, especially at the start, should be the absolute minimum required. A speed of 400 rpm was satisfactory during the trials reported here.

Broader conclusions are that this general approach of assessing electrostatic hazards in a range of process operations by a combination of experimental measurements and computer modelling provides an effective way of avoiding the need for sometimes onerous fire and explosion prevention and/or protection measures, while still providing a demonstrably safe working environment for personnel.

In the present case the alternative would indeed have been onerous. A first estimate of the capital cost of replacing the currently used vessel with one suitable for inert gas blanketing, and provision of the necessary nitrogen supply, was about £250,000. There would also be ongoing consumables and maintenance costs associated with the new equipment. Apart from the cost, there are safety implications with inerting. As a means of controlling fire and explosion hazards it must never be thought of as a simple or trivial solution. The potential hazards introduced by the use of inert gas blanketing can require significant changes in working practices simply to ensure continued operator safety.

At the moment, almost every time the type of technique described in this paper is used, a new way of combining the measurements with modelling must be developed. However, with increasing use across a range of process operations, the tools required will become increasingly familiar, making this an effective, valuable and increasingly common approach to fire and explosion hazard assessment.

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