# Reduction of Condensate Residues in the Reflow Process by Targeted Control of Chemical Reactions

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## ABSTRACT

Increased electronics manufacturing results in an increased amount of condensate residue. The problem is not only to meet the increased cleaning requirements with increasing production, it is much more the absence of knowledge about the condensate residue formation process and how this residue can be minimized and inhibited in its formation. Some of the substances in the condensate residue are harmful to health. They cause skin irritations and allergic reactions. Some of them contaminate the environment as toxic hazardous waste. Therefore, this paper focuses on the reduction of condensate residues from a soldering process based on previous white papers “Detailed Study of Condensate Residues in the Soldering Process – Analysis of the Responsible Reaction Partners as Well as Reasons for Condensate Polymerization and Growth of Crystalline Structures” and “Molecular Fingerprint of Condensate Residues in the Soldering Process – Detailed FT-IR Spectroscopic Analyses and Identification of Reaction Partners” presented at SMTA International Conference in 2021 and 2023.

After theoretical study of the formation process and FT-IR spectroscopic analyses of the condensate residues, substances were identified that play a significant role in condensate formation. Three of these substances need to be highlighted: Rosin from the solder paste, photo initiator from the solder mask and Triaminotriazine from the PCB substrate. Based on these results, experimental tests were performed with condensate residue samples from soldering process and reaction partners that were identified as potentially effective in inhibiting polymerization, cross-linking reactions and crystallization processes.

Condensate residue components can be physically and chemically bound and selectively modified. This allows the inhibition of polymerization and cross-linking processes, the reduction of crystalline growth and the effective control of chemical reactions. For the experimental procedures, samples of various condensate residue from the soldering process were combined with the reagents and were then subjected to a thermal process. The following FT-IR analyses enable the identification of the resulting reaction products. This allows the visualization of the chemical changes and helps to understand the chemical reaction processes.

Important conclusions can be drawn as a result. Experiments have shown that it is possible to successfully modify crystalline structures of the photo initiator in the condensate residue by a specific chemical reaction, and thus inhibited crystalline growth. It is also possible to modify the polymerization and crosslinking behavior of rosin in the condensate residue in so far that a crosslinking reaction can be effectively inhibited. This work is therefore another important step on the way to sustainable electronics production, increasing maintenance cycles combined with reduced cleaning requirements.

Key words: condensate residue, condensate formation, condensate analyses, reflow process, soldering, solder paste, PCB

## INTRODUCTION

Condensate residues affect maintenance intervals in electronics production. They can trigger allergic reactions of service engineers and contaminate the environment as toxic hazardous waste. If they remain uncleaned or insufficiently cleaned on the surface of the circuit board, they can result in electromigration and thus lead to product failure. Previous work on condensate such as “Detailed Study of Condensate Residues - Analysis of the Responsible Reaction Partners as well as Reasons for Condensate Polymerization and Growth of Crystalline Structures in the Soldering Process.” and “Molecular Fingerprint of Condensate Residues in the Soldering Process - Detailed FT-IR Spectroscopic Analyses and Identification of Reaction Partners” discussed in detail condensate residue formation mechanisms[1] and identified components of condensate residues. This work is the basis for the next step - a targeted condensate modification on a chemical level. The goal is the realization of a controlled chemical manipulation that will help to inhibit polymerization and cross-linking processes and minimize crystal growth. As a result, maintenance intervals can be extended and condensate residues can be removed more easily.

## TESTS

For the tests, condensate samples from a reflow process were collected from the inlet zone, the peak zone and the cooling zone at regular machine maintenance and cleaning intervals. The condensate samples were stored in 15 ml airtight laboratory vials immediately after collection to minimize the influence of oxygen and humidity.

FT-IR spectra of the respective condensate residue samples were performed (Figure 1). The molecular fingerprint was determined using a Bruker spectrometer, type Tensor 27. For the FT-IR analyses, the respective condensate sample was extracted from the airtight vial and placed on the measuring cell (Pike Miracle, ZnSe optics) of the FT-IR spectrometer for analysis. The analyses of the spectra enabled a clear identification[2] of the main components of the respective condensate samples (Table 1). The condensate residue from the inlet area of the reflow machine contained mainly a photo initiator "2-methyl-4'-(methylthio)-2-morpholino-propiophenone", abietic acid of the rosin and triaminotriazine, in a lower concentration than in the condensate from the cooling zone. The condensate residue from the peak zone mainly contained abietic acid from the rosin.

This substance is contained in rosin-based solder pastes and becomes gaseous at 139°C-165°C. The condensate from the cooling zone had crystalline structures and mainly contained triaminotriazine and abietic acid from the rosin. Triaminotriazine is a component of the printed circuit board and the solder resist. Triaminotriazine in particular is a substance that cross-links under the influence of temperature. This cross-linking reaction takes place in the soldering machine as soon as suitable temperatures are present. The cross-linking temperature window is above 250°C to approx. 360°C [3].

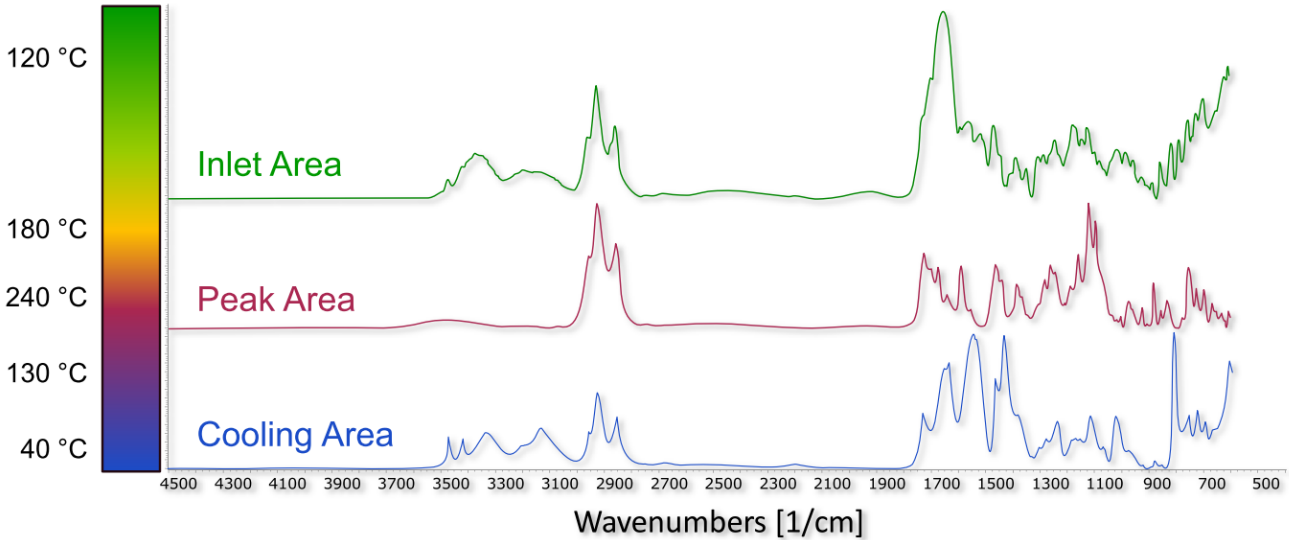
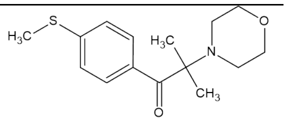
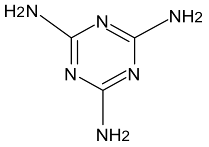
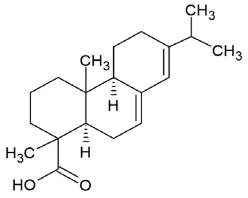


**Figure 1.** FT-IR Spectra of Condensate Residues from Reflow Soldering Process

**Table 1.** Identified Condensate Components from the Respective Extraction Area in a Reflow Machine

| **Condensate Residue Extraction Area** | **Identified Components** |
|---|---|
| Inlet Area | Photo Initiator "2-methyl-4'-(methylthio)-2-morpholino-propiophenone"<br>Triaminotriazine<br>Abietic Acid (Rosin) |
| Peak Area | Abietic Acid (Rosin) |
| Cooling Area | Triaminotriazine<br>Abietic Acid (Rosin) |

**Table 2.** Chemical Structure of Identified Components

| **Identified Components** | **Chemical Structure** |
|---|---|
| Photo Initiator "2-methyl-4'-(methylthio)-2-morpholino-propiophenone" |  |
| Triaminotriazine |  |
| Abietic Acid |  |

Based on the identified substances in the condensate residues (Table 2), three potential reaction partners were selected. The purpose of the experiments was to start specific chemical reactions in order to minimize certain areas in the spectrum of the respective condensate sample or to modify them in a way that, for example, inhibits the growth of crystalline structures. Polymerization and cross-linking processes should also be inhibited.

For the experiments, equal amounts of condensate residues from each zone of the reflow machine were mixed with reactants A, B and C in a ratio of 3:1. These were covered with aluminum foil in 15 ml laboratory vials and then sealed airtight. The condensate residue samples were placed in the oven at 170°C for 60 minutes. The temperature was selected so that the rosin contained in the condensate residue became gaseous, but without stimulating further thermal degradation and the resulting polymerization and cross-linking reactions. The reagents reacted with the respective condensate samples under the influence of temperature. Gaseous components could condense on the surface of the aluminum foil (Figure 2). In this way, these residues could also be analyzed using the FT-IR spectrometer.

**Figure 2.** Condensate Samples with Reagents A, B, and

## RESULTS

Figure 3 shows FT-IR spectra of the condensate from the inlet area after their reaction time with substances A, B and C. The main substances identified here were triaminotriazines, rosin and the photo initiator “2-methyl-4'-(methylthio)-2-morpholino¬propiophenone”. The region characteristic of triaminotriazines in the spectrum of the condensate (dashed marked area) remains clearly visible in samples treated with reagents A and B. The sample treated with reagent C shows a clear change. This change is not limited to the characteristic triaminotriazine region, but affects the complete spectrum.

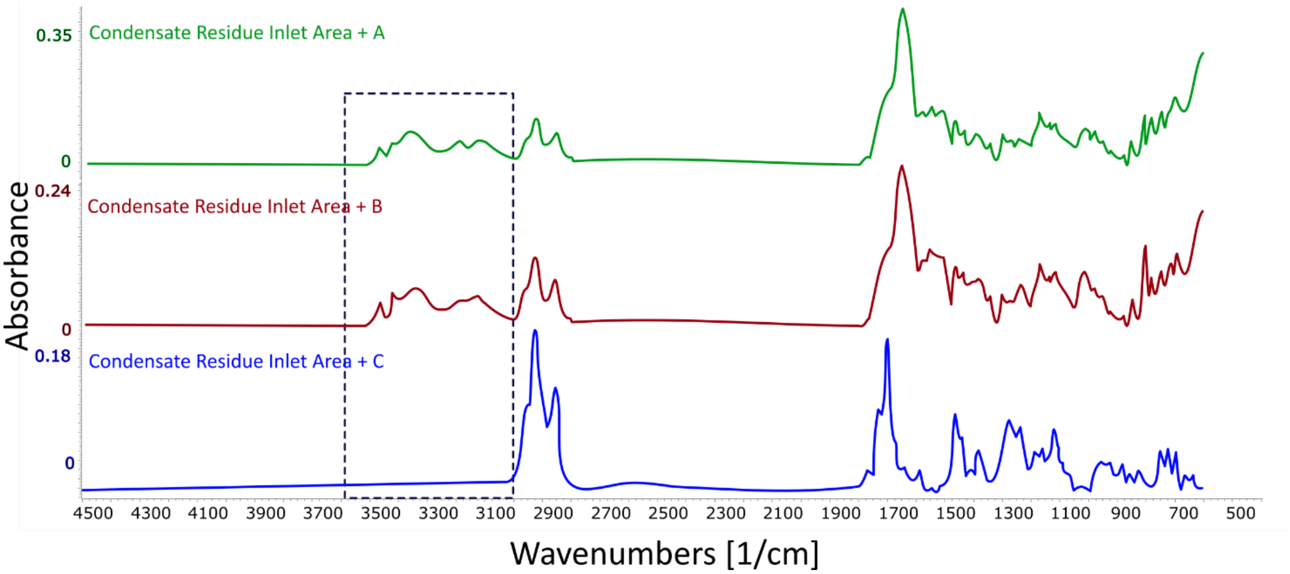


**Figure 3.** Spectra of Condensate Residues from Inlet Area treated with Reagents A, B and C

While reagent C triggered a significant change in the spectrum of the condensate sample, the condensed residues on the aluminum foil showed a different behavior (Figure 4). Here, reagent B was most effective, as it resulted in the smallest amount of residue condensing on the aluminum foil.

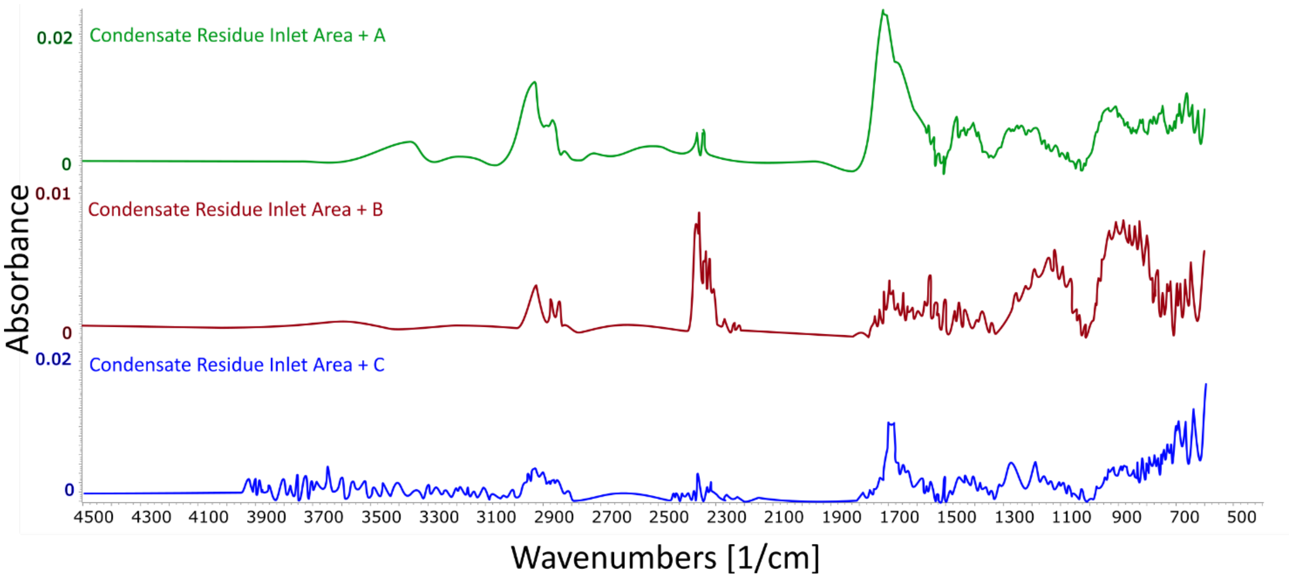


**Figure 4.** Spectra of Condensate Residues from Inlet Area treated with Reagents A, B and C – Condensation on Aluminum Foil

The spectrum of the condensate from the peak area mainly contained abietic acid from the rosin. Here, the spectrum shows great similarities for all reagents (Figure 5). Only with reagent A are there slight differences both in the peak intensity and in the overall spectrum.

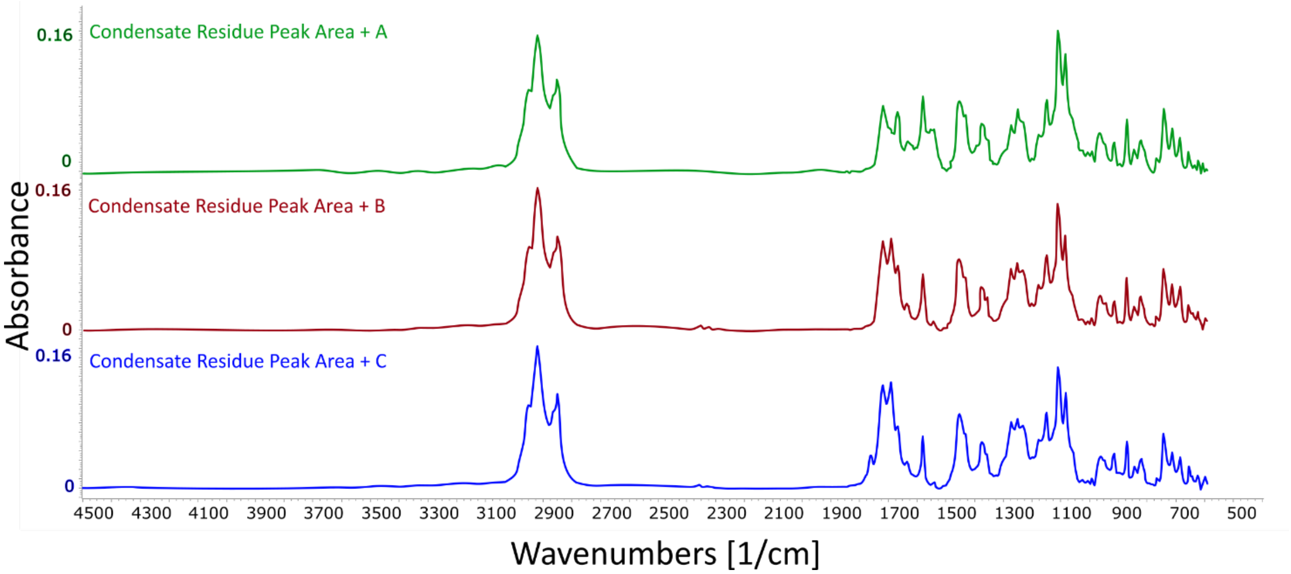


**Figure 5.** Spectra of Condensate Residues from Cooling Area treated with Reagents A, B and C

Figure 6 shows spectra of condensate residues from peak area of the soldering machine, condensed on aluminum foil, treated with reagents A, B and C. Like the condensate sample from the inlet area, reagent B shows the best results for the residues condensed on the aluminum foil. The lowest condensed residues are found here.

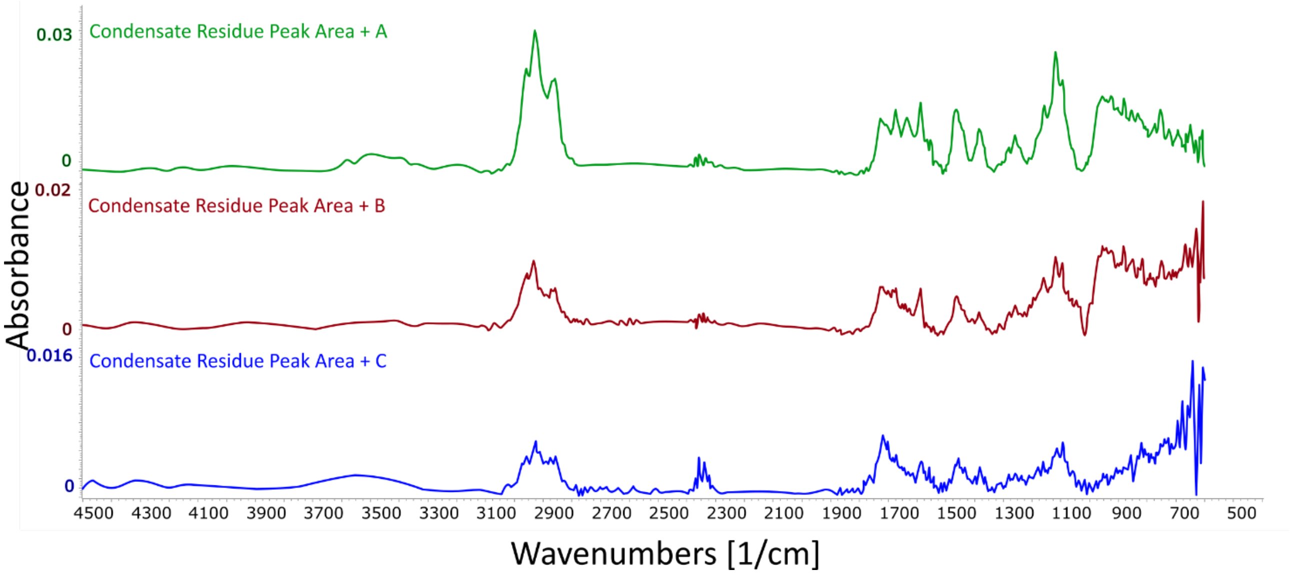


**Figure 6.** Spectra of Condensate Residues from Peak Area treated with Reagents A, B and C – Condensation on Aluminum Foil

The condensate spectrum from the cooling range clearly shows a change in the spectrum with reagent C (Figure 7). The region in the condensate spectrum that is characteristic of triaminotriazines (dashed marked area) has almost completely disappeared. The spectrum is significantly different from the condensate spectra with reagents A and B. These both look almost identical. Only the intensity (the height of the peaks) is significantly lower in the sample treated with reagent A.

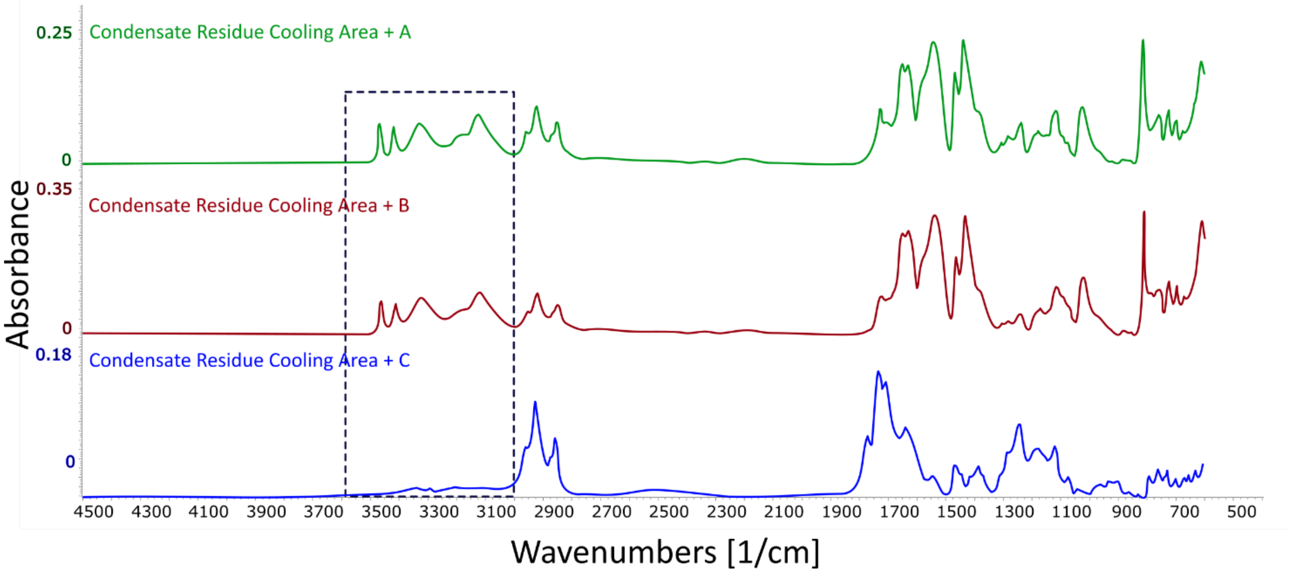


**Figure 7.** Spectrum of Condensate Residue from Cooling Area treated with Reagents A, B and C

Reagent B performed the best result on the aluminum foil, as was already shown for the other two condensate residue samples from the inlet area and the peak area (Figure 8). The peak intensity is lowest here.

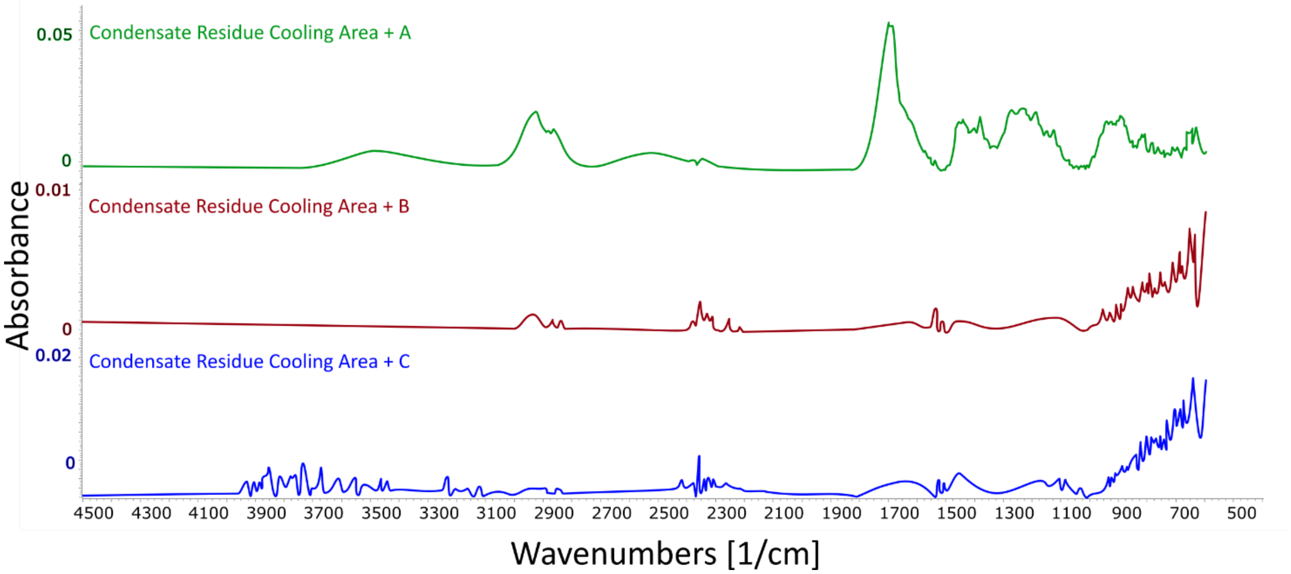


**Figure 8.** Spectra of Condensate Residues from Cooling Area treated with Reagents A, B and C – Condensation on Aluminum Foil

**Table 3.** Chemical Effectiveness on Condensate Residue

| Reagent | A | B | C |
|---|---|---|---|
| Inlet Zone | | | X |
| Peak Zone | X | | |
| Cooling Zone | | | X |

Table 3 shows the effectiveness of reagents A, B and C on the change in spectra of the condensate samples. Table 4 shows the effectiveness of reagents A, B and C on the peak intensity of the condensate samples. The lower the peak intensity, the lower the concentration of condensed residues on the aluminum foil.

**Table 4.** Minimal Condensate Residue on the Aluminum Foil

| Reagent | A | B | C |
|---|---|---|---|
| Inlet Zone | | X | |
| Peak Zone | | X | |
| Cooling Zone | | X | |

**Reaction process based on the example of the chemical class of reagent C**

For a better understanding of the occurring reactions, an example reaction with the condensate sample from the cooling area with a chemical class of reagent C - citric acid - is discussed in more detail here. Under the influence of temperature, a thermal decomposition of the citric acid initially takes place at 170-175°C. This leads to the separation of $H_2O$ and the formation of aconitic acid (Figure 9). In the further process of the reaction, the aconitic acid decomposes into aldehydes, ketones, unsaturated compounds and low-molecular acids (Figure 10). All these compounds can now start chemical reactions with the condensate residue from the cooling zone of the reflow machine.

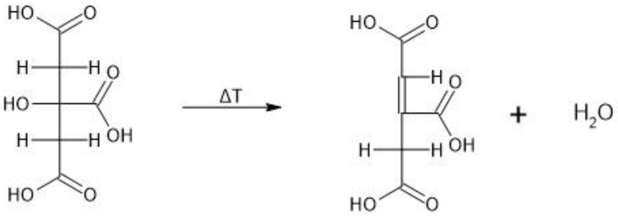


**Figure 9.** Thermal Degradation of Citric Acid – Formation of Aconitic Acid

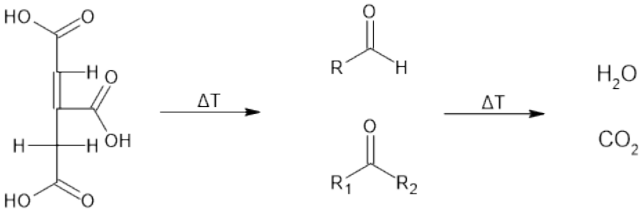


**Figure 10.** Decomposition of Aconitic Acid into Aldehydes and Ketones

Triaminotriazine is an aromatic compound with a hexagonal, cyclic structure at its core, in which single and double bonds alternate. The special feature of triaminotriazines is their high nitrogen content. Not only are three of the six constituents of the ring structure nitrogen atoms, but the free bonds of the three carbon atoms are also each occupied by a nitrogen-containing amino group. The high nitrogen content gives triaminotriazine its fire-retardant properties, among other things.

In general, triaminotriazine is chemically very stable and at temperatures above 250°C this only leads to further cross-linking with the separation of ammonia (Figure 11). Significant degradation by pyrolysis only takes place above 400°C [4].

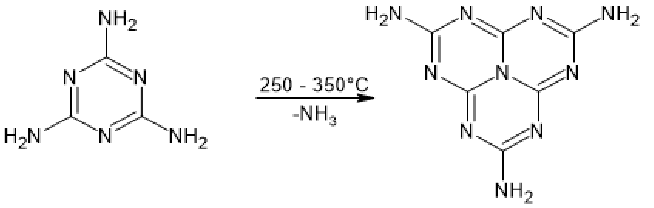


**Figure 11.** Cross-linking Reaction of Triaminotirazine with Separation of Ammonia

The goal is therefore to prevent the cross-linking reactions significantly by removing the amine groups ($NH_2$). Triaminotriazine reacts with strong acids and oxidizing agents. It neutralizes acids by releasing heat and forming salts and water. This can be realized by citric acid as well as by its reaction products. The $NH_2$ groups are largely eliminated by the reaction with aldehyde and ketone compounds (through the thermal degradation of citric acid). In the further reaction process, the reaction product can react with citric acid and is no longer available for a further cross-linking reaction with free triaminotirazines (Figure 12).

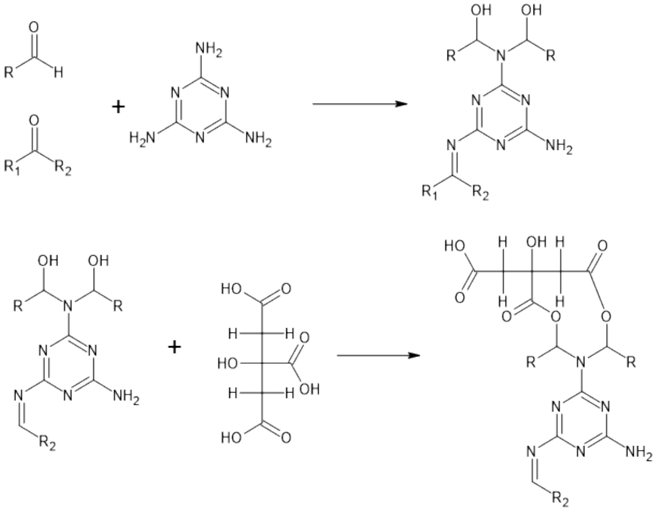


**Figure 12.** Reaction of Triaminotriazines with Ketone and Aldehyde Compounds from Citric Acid. Subsequent Reaction of the Reaction Product with Citric Acid Prevents a Cross-linking Reaction of Triaminotriazine.

## CONCLUSION

In summary, it could be shown under laboratory conditions that it is possible to influence chemical processes in the condensate residue and to inhibit polymerization, cross-linking reactions and crystallization processes.

Reagent A led to a peak reduction and moderate changes in the spectrum of the condensate sample from the peak range. While reagents B and C did not trigger any visible change in the spectrum. On the one hand, this may be due to the fact that reagent A was specifically selected for chemical manipulation of the cross-linked rosin components, where substances B and C are chemically less effective. On the other hand, condensate from this area of the reflow machine was subjected to a so-called pyrolysis, which already led to a similar change in the chemical structure as in a reaction with reagent A.

While reagent B showed no clear effect on the chemical reaction in the condensate samples from the inlet area, the peak area and the cooling area, this substance resulted in a reduction of the peaks in the spectrum. The analyses of the condensed reaction products on the aluminum foil confirmed this. The lowest condensed traces were present in all condensate samples. Substance B shows very good absorbing behavior. It can be used in addition to reagents A and C to absorb gaseous reaction products.

Reagent C showed an effective chemical change in condensate samples from the inlet and cooling areas. This was clearly visible in corresponding spectra. An exemplary reaction process from the family of reagent C - citric acid illustrated the mechanism of action.

## REFERENCES

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