Quality Control of PVC Stabilisers by ATR-FTIR Spectroscopy - A Kind of Magic?

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Abstract: *Polyvinyl chloride (PVC) is one of the most widely used plastics in the world. However, its processing differs from that of other polymers because PVC decomposes under the influence of shear and heat. In aaorder to ensure processing without problems and optimal properties of the final product, the addition of so-called PVC stabilisers is absolutely necessary. These stabilisers are complex mixtures of metal soaps, acid scavengers, antioxidants, co-stabilisers, color improvers, lubricants, etc. Up to 20 additives can be present in this mixture. This makes quality control a challenge. In addition to many other methods that can only analyze individual aspects of the complex mixture, ATR-FTIR spectroscopy is slowly beginning to gain acceptance. In our paper, we will demonstrate that ATR-FTIR spectroscopy is only slightly or not at all suitable for quality control of powdered, complex mixtures. They can be used in PVC pipes, fittings, profiles, decorative panels, boards, shutters, wire & cables, etc. applications.*

Key Words; *Polyvinyl Chloride, Stabilizers, Thermal Stability, Degradation and ATR-FTIR*

1. Introduction ;

1.1 Polyvinyl Chloride (PVC);

Polyvinyl chloride (PVC) is probably one of the most fascinating, most versatile, and oldest thermoplastic polymers. PVC is the third most important polymer for plastics after polyethylene and polypropylene. On July 04th in 2023 the scientific base of its production was 110 years old PVC is the polymer with which a person comes into contact within minutes of their birth: the bracelet bearing a newborn's name and birth date is commonly made of PVC. Pipes, fittings, profiles (for example for windows), pharmaceutical films, sheets (foamed or compact) are made from rigid PVC. Soft PVC plays a role in cable applications either as Isolation or sheathing plays an important role and is also used in floor coverings, hoses, shoe soles, membranes for roofs, ponds, tunnels…

However, the processing of PVC is somewhat more complicated than that of polyolefins because, as in most polymers, the PVC chain is not without defects. The most important defects are

- tertiary chlorine atoms, which result from branch formation during polymerization, and
- allylic chlorine atoms, which form for example by termination of the polymerization reaction [1]

PVC is therefore very sensitive to heat and shear. The degradation of PVC [2-8] starts at these defect sites. Therefore, these chlorine atoms are also called labile chlorine atoms, and the site of the defect is called the initiation site of degradation. The degradation of PVC is called dehydrochlorination because hydrochloric acid (hydrogen chloride, HCl) is split off during the process. The split-off of HCl generates new defects. If no stabiliser intervenes, this process continues in a zipper-like fashion. Hydrochloric acid and conjugated double bonds form; the latter are also called polyene sequences.

Once six to seven conjugated double bonds have formed, a slight yellowing of the PVC can be observed. This yellow discoloration grows darker with increasing length of conjugation, from red to brown and finally to black. The PVC is then called burnt. [1]. That's why the addition of heat stabilisers (and lubricants) are absolutely necessary. Stabilisers [2-8] in this sense are not single chemical substances. These are blends of minimum two to up 25 ingredients. Each of it has at least one special function for processing of PVC products. Most the ingredients have more than one function, and in some cases some negative side effects [9]. They are also called onepacks. In most instances stabilizer blends are required to achieve the optimal PVC processing performance and the best properties for the final product. Further functions of the additives are

- substitution of labile chlorine atoms,
- shortening of polyene sequences,
- neutralization of HCl, and
- prevention of autoxidation.

These one-packs have the following advantages:

- All components (acid scavengers, metal soaps, lubricants, flow modifiers, and other components) are included. In many instances, the onepacks are tailor-made, individual solutions.
- The cost of quality control is significantly lower because only one raw material, the one-pack, and not the individual additives, have to be tested.
- The stock-keeping is much simpler, as is the dosing and mixing in production.
- Any variability of the blends is reduced due to the fact that the minor components, the single additives, are preblended. A weighing error of the preblend has a much smaller effect compared to an error made with a highly lubricating single additive.
- Low-dust or dust-free one-packs improve plant hygiene for transport and mixing.
- Less packaging material is generated.
- The costs for new developments are lowered.
- In addition to one-pack deliveries, the one-pack supplier also ensures competent service [1].

1.2 Quality Control of PVC Stabilisers; [9]

Today the complete quality control (QC) of such a complex mixture is theoretically possible but not economically feasible. In the past it was much easier. Stabilisers [2-8] were based on toxic meals like lead. The rule of thumb said that the higher the lead content, the higher the heat stability when processing the blends at temperatures mentioned before. Lead content can be accurately and directly analyzed by several methods. A different method is to burn the lead stabiliser under controlled conditions. The left material is called residue on ignition or ash content. This is when the first inaccuracies creep in, because the presence of other metal compounds results in a higher ash content. In addition, recent developments in hybrid lead stabilisers with lower lead content have shown that the same heat stability can be achieved by using synergists. This means that measuring the lead content is obsolete.
In the case of lead-free stabilisers, this gets even more complicated because a variety of elements are included: sodium, magnesium, calcium, aluminium, silicon and zinc. For the sake of simplicity, let's

only consider the elements calcium and zinc. On the one hand, they have different effects on heat stability. Zinc reduces it but is essential for some stabilisers because zinc compounds result in whiter color of end product. Unfortunately, this does not apply to all zinc compounds. Calcium, for its part, reduces the whiteness of the end product but improves heat stability in most, but not all cases. On the other hand, neither the calcium nor the zinc content says anything about the "origin" of its presence. Calcium occurs in at least five common components of the blend and zinc in at least four. It is true that all of these elements can be analyzed relatively cheaply and accurately these days, but even an expert cannot get any conclusions about the quality of the stabiliser [2-8] mixture based on these values. Therefore, the analysis of the metals is actually useless.

In order to get useful information about the quality of stabiliser, All the components must be analyzed in detail. This is associated with a very high expenditure of staff, material and time, which very quickly ends up in costs of several thousand Euros. In addition, the investment costs to set up the analytical equipment are very high. Well-trained staff is needed and finally a specialist who can interpret the information. No customer wants to and will pay for this effort.

Another important parameter is the “loss on dry” (LoD) of the stabiliser, because the water inside the blend can increase the frequency of stopping and cleaning the production line. Therefore the sample is heated to 105°C. In the case of lead stabilisers, the result is correct in most cases. The lead-free alternatives may contain substances that thermally degrade or that react with each other or that contain volatile organic substances. As a result, a value higher than the actual water content is measured.

So far we have only looked at two properties of the PVC product: its color and heat stability. But there are other properties which are difficult to predict based on a full chemical analysis, such as gloss, mechanical or electrical properties, light stability etc.

Therefore, it would theoretically make sense to test the stabiliser [2-8], as completely as possible, in an application laboratory. After all, the PVC processor does not buy lead, calcium, zinc or any other element. A processor buys "Performance", which guarantees problem-free processing and a high-quality end product with a long-life cycle. An investment in a high-performance application laboratory is in the range of several 100’000 Euros. A well-trained, experienced staff is again required. The cost of materials is 10 to 50 times higher than the amount of heat stabiliser used. In contrast to the above analytical methods, which provide absolute and reproducible results, most performance tests are relative methods. This means that at least one and in some cases several so- called references from previous investigations must investigated again. The costs will go ballistic, due to which all stabiliser manufacturers limit the number of tests as much as possible, and use methods which are simple and cheap in the application laboratory. However, this significantly limits the informative value of such tests.

However, some converters consider FTIR spectroscopy as the non plus ultra. In this paper we will share the results of our test and show the limitations in the QC of PVC stabilisers.

1.3 Infrared (IR) Spectroscopy;

Infrared spectroscopy, or IR spectroscopy for short, is a physical analysis method that works with infrared radiation.

Nowadays, Fourier transform infrared spectrometers (FTIR spectrometers) are mainly used. These offer some decisive advantages over the dispersive spectrometers that were previously common. For example, FTIR spectrometers have a significantly higher signal-to-noise ratio and require significantly shorter measurement times.

ATR infrared spectroscopy (attenuated total reflection) is a measurement technique in infrared spectroscopy (IR spectroscopy) for examining the surfaces of opaque materials [10] such as paint layers or polymer films and also liquid samples such as solvent mixtures. The method was first introduced by Harrick in 1960 [11] and Fahrenfort in 1961 [12]. The intensity of the reflected light is measured, which allows conclusions to be drawn about the absorbing medium.

While IR spectroscopy was previously used for the qualitative analysis and characterization of known and unknown substances, it is now also used for the quantitative determination of known substances, the identification of which is carried out using a reference spectrum.

With a sufficiently good calibration, quantitative measurements of substances and mixtures of substances are also possible with great accuracy [13-16]. A somewhat simplified technology consists in superimposing the spectrum of a mixture of substances with a reference spectrum of a mixture of substances and calculating the regression value. This technology is also used in the PVC processing industry for QC on stabilisers.

The aim of this work is to investigate whether ATR-FTIR spectroscopy is a suitable method for QC of solid, powdered multicomponent mixtures.

2. Experimental;

2.1 Materials;

Following raw materials were used in this study:

- Polyvinyl Chloride (PVC) from Formosa Plastics Corporation: suspension grade S-65D, which K-value is 65.7 to 67.1.
- Uncoated calcium carbonate from RK Trading grade A5, which whiteness has 98.42% and a sieve residue of <0.1% at 45 micron.
- Calcium stearate from Platinum Polymer Additives Pvt. Ltd., grade is calcium stearate (PVC) with a melting point of 160 to 180°C, an ash content 9.1 to 11.2% and a sieve residue of <2.0% at 45 micron.
- Calcium Acetylacetonate (Caacac) from Agrifarm Protection Co., Ltd., China with melting point of 275 to 280°C, a calcium content of 16.6 to 17.5% and a sieve residue of <0.1% at 45 micron.
- Zinc stearate from Platinum Polymer Additives Pvt. Ltd., India, grade is zinc stearate (PVC) with a melting point of 115 to 130°C, an ash content 12.4 -14.9 % and a sieve residue of <2% at 45 micron.
- 4A-Zeolite powder from SILKEM, Slovenia, grade ZP-4A-TSR with an ash content (1h/800°C) of 78-82% and a sieve residue of <0.1% at 45 micron.
- Magnesium hydroxide from Quimica Del Rey, S. A. DE C. V., Mexico, grade is HYDROMG DT containing 99.2% magnesium Hydroxide and a sieve residue of <0.1% at 45 micron.
- Pentaerythritol from LCY Chemical Corp., Taiwan purity min. 98%, melting point min. 250°C and a sieve residue of <0.1% at 63 micron.
- Tris(2-hydroxyethyl) isocyanurate (THEIC) from Sunshield Chemical Ltd., India, grade SUN THEIC POWDER with a melting point of 133 to 137°C and a sieve residue of <0.1% at 200 micron.
- High density polyethylene wax from Marcus Oils & Chemicals Pvt. Ltd., India, grade iPR-700 with a dropping point 100 ±5°C.
- Nonpolar low density PE wax AC 617 from Honeywell, USA with a density of 0.91 g/mL and a dropping point of 101°C.

- Oxidised high density polyethylene wax from Honeywell AC 617, USA with a dropping point of 135 to 140°C, a density of 0.98 g/mL, an acid value 16 mg KOH and a sieve residue <0.01% at 420 micron.

2.2 Methods;

Following methods were applied:

- High Speed Lab Mixer from Shree Radhe Krishna Extrusions Pvt. Ltd., India, model JJH-05 with a maximum speed of 1400 rpm. The mixer was set up to 120°C, raw materials were filled in, mixer was closed and started. Dryblend was discharged at 120°C on a tray and cooled to room temperature. Dryblend was resting minimum 12 hours before other investigations.
- Torque Rheometer from Harbin Hapro Electric Technology Co., Ltd., China RM-200C, model MIX-60C. Sample weights are 68 gm, chamber temperature temperature 170°C, 45 rpm for 5 minutes.
- Single screw extruder from Aasabi, India, set temperature of barrel is 155-170°C, 60 rpm and average out is 7 kg/h.
- Testing Oven from Harbin Hapro Electric Technology Co., Ltd., China, chamber temperature 190°C, 120 min.
- Colorimeter from Shenzhen Wave Optoelectronics Technology Co. Ltd., China, model WR-10 for measurement of CIELab colour.
- ATR-FTIR from SHIMADZU CORP., Japan, model IRSpirit-X

3. Results and Discussion;

3.1 Repeated ATR-FTIR Measurement of a Powdery Mixture with 10 Additives;

3.1.1 Entire range of wave numbers;

In the first step, a mixture[1]* (XP24-001 GJ) with a known composition of calcium stearate, zinc stearate, Antioxidant 76, zeolite, pentaerythritol, calcium acetyl acetonate, calcium carbonate, an HDPE and an oxydised HDPE waxes is produced. Ten samples were taken from this mixture and measured using ATR-FTIR. We arbitrarily chose one of these spectra (XP 24-001 GJ Std; Figure 1) as a reference spectrum for regression analysis with the others and calculated the Purity indexs. The results are summarized in Table 1.

The purity index (P) indicates the degree and extent of agreement between two spectra. It is determined by the least squares fit coefficient, which is calculated for each pair of intensities of the two spectra to be compared. The purity index lies between 0 and 1. Zero means absolute dissimilarity between two spectra, and 1 means that the two spectra are identical [17].

Unexpectedly, the purity indices (after normalisation) in Table 1 vary only slightly. The average value is 0.9982 in a range of 0.9957 to 0.9993. The same applies to the slope of the line that compares the spectrum of the reference with that of the current sample. This should be one for a very good correlation. The intersection of this line with the y-axis should be zero. The slope varies between 0.9806 and 1.0393 with a mean of 1.0178. At the intersection, the mean is 0.0034, the minimum is - 0.0012 and the maximum is 0.0070. This indicates that the reproducibility of the measurements is very good to excellent. We did not expect this because, on the one hand, the sample quantity is very small at 5 to 10 mg [14]. This is extremely small compared to other wet chemical methods, for

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1* The exact composition is a trade secret of Platinum Industries Ltd. and corresponds to a commercially available stabiliser.

example, where the sample quantity is 2 grams. On the other hand, it is a powdery multi-component mixture with powders of very different grain size distributions. We actually expected inhomogeneity in the micro range due to these different grain size distributions.

While the zeolite has a grain size distribution of <1 to ~12 microns (Figure 2), that of calcium stearate (Figure 3) is in the range of <1 to ~60 microns (both measured under the same conditions in water and evaluated in volume mode). We do not have a typical particle size distribution for the oxidized HDPE wax. However, the manufacturer states that the sieve residue is 0 at 420 microns. This means that the mixture examined contains particles of <1 micron to >400 microns.

Urvadi etal. [16] worked on „Different particle fractions of common minerals which „…were prepared in order to demonstrate that ATR FT-IR spectra of common rock-forming minerals, besides other factors (i.e., grain shape, structural changes, band overlaps, multiple scattering), depend primarily on the particle size. The results show that the positions of the most intense bands shift to higher wavenumbers when the particle size decreases. This difference in wavenumbers is clearly less than 1 cm^{-1}. Additionally, the coarser the mineral particles, the broader the widths of the IR bands, regardless the degree of crystallinity and particle shape. The intensity and area of IR bands gradually increases from coarser particles up to 2–4 mm where the absorbance is at maximum. However, a drop in the intensity and band areas of minerals is found if the particle size is smaller (<2mm) than the average penetration depth of the IR light and reaches a value that is determined by the wavelength of the IR light. Therefore, fine particles should be carefully evaluated using ATR spectroscopy as their real proportion may be underestimated in particulate materials unless they have very similarly small particle size (i.e., similar state of aggregation). Furthermore, the nonlinear relationship between the median diameter of various particle size fractions and max- imum IR band absorbance are the same as for particle size and surface area. Therefore, particle size and surface area is experimentally revealed to be the principal factors determining modal compositions of powdered samples with substantially different particle size. A larger band area of water (3000–3620 cm^{-1}) is detected in powder below 2 mm in diameter than in the other particle size fractions due to the higher specific surface of particles. It is also concluded that at least a proportion of the moisture could be very adhesive to the particles due to its band shift towards lower wavenumbers.“

It should be noted that normalisation of the spectra is advantageous. In a range of 2300 to 2400 1/cm we observed from time to time a double band. This band is most likely due to the asymmetric stretch oscillation of adsorbed carbon dioxide [18], which might distort the purity index if not known.

Table 1 :- Measured ATR-FTIR spectra (400 to 4000 1/cm) and their Purity index P with the reference spectra XP 24-001 GJ Std (with normalisation at maximum intensity, no smoothing, threshold = 0.95)

Code of the spectra	**Purity index**	**Slope**	**Intercept**
XP 24-001 GJ Std.	Reference		
XP-24-001-GJ-Sample 2	0,9993	1,0198	0,0011
XP-24-001-GJ-Sample 3	0,9991	1,0393	0,0037
XP-24-001-GJ-Sample 4	0,9985	1,0215	0,0064
XP-24-001-GJ-Sample 5	0,9989	1,0030	0,0053
XP-24-001-GJ-Sample 6	0,9975	1,0217	0,0046

Code of the spectra	Purity index	Slope	Intercept
XP-24-001-GJ-Sample 7	0,9983	1,0237	0,0033
XP-24-001-GJ-Sample 8	0,9957	0,9806	0,0070
XP-24-001-GJ-Sample 9	0,9989	1,0346	-0,0012
XP-24-001-GJ-Sample 10	0,9974	1,0162	0,0002
Average	0,9982	1,0178	0,0034
Minimum	0,9957	0,9806	-0,0012
Maximum	0,9993	1,0393	0,0070

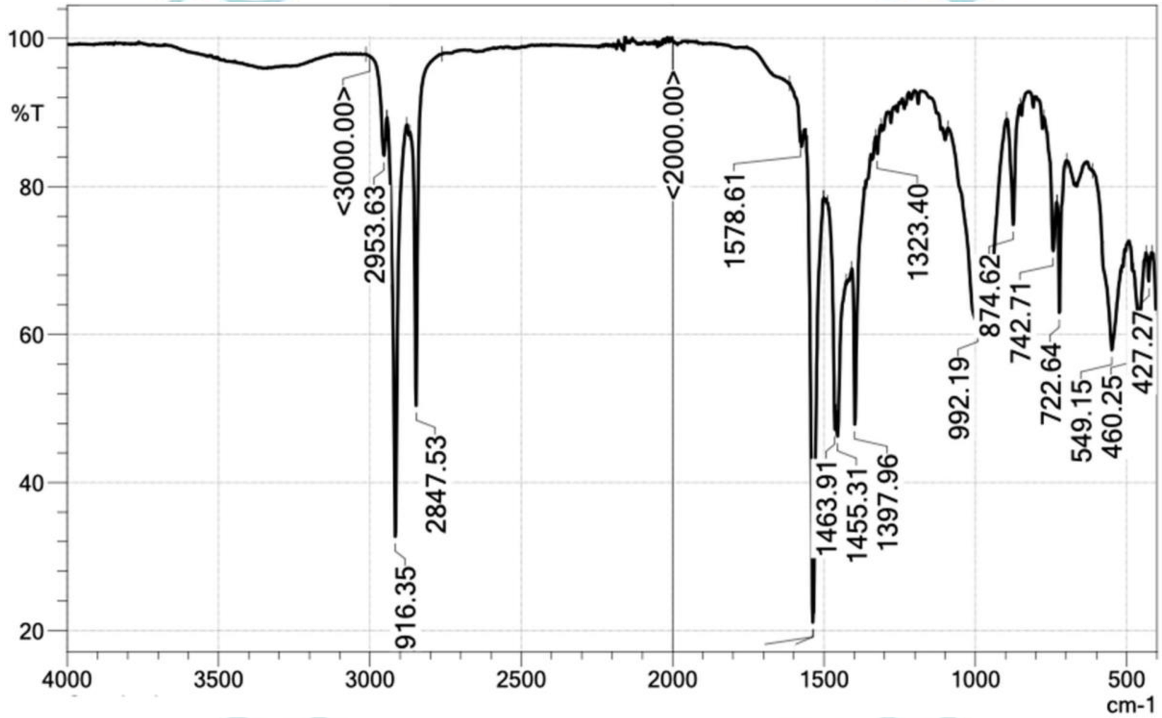

Figure 1:- ATR-FTIR spectra of XP24-001 GJ Std.

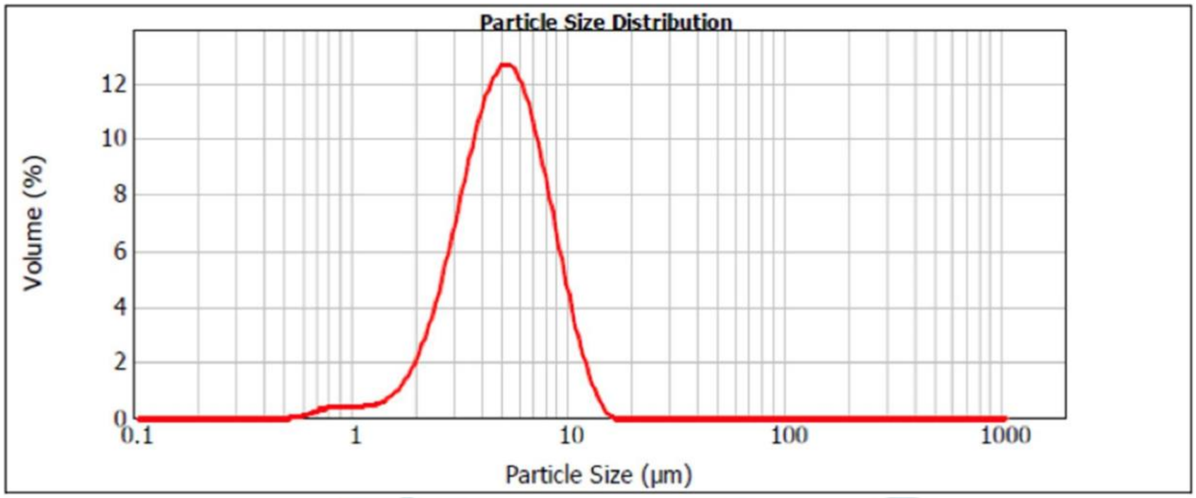

Figure 2:- Particle size distribution of zeolite in water and with volume mode; D10%: 3.0; D50%: 5.0, D98%: 11.7

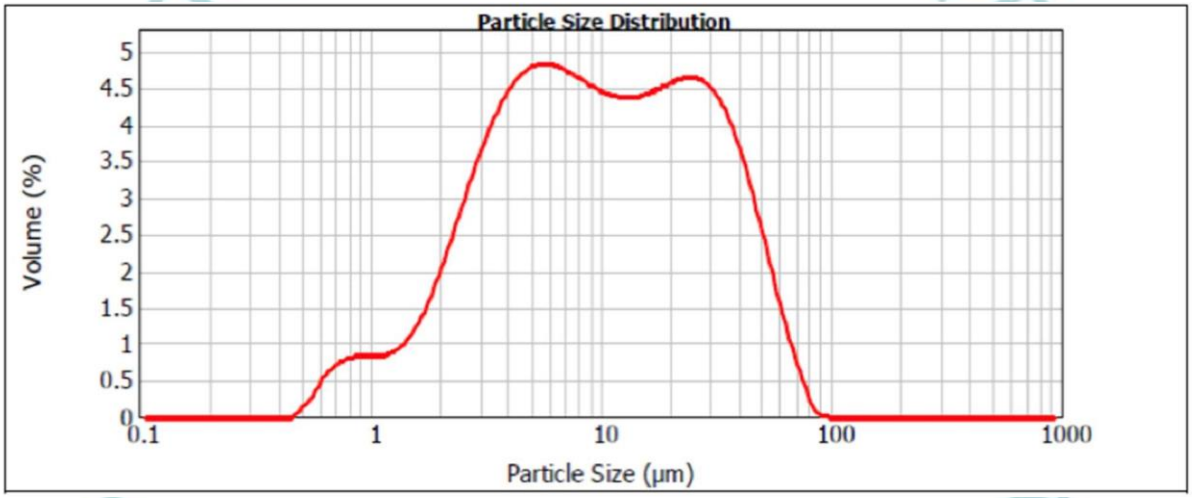

Figure 3:- Particle size distribution of calcium stearate in water and with volume mode; D10%: 2.3; D50%: 9.6, D98%: 58.5

3.1.2 Slightly extended fingerprint range of wave numbers

The so-called fingerprint is located in the IR spectrum below 1500 1/cm. In this range, individual substances can be clearly identified... Therefore, we cut off all wave numbers above 1600 1/cm in the existing spectra to determine the purity index. We chose <1600 1/cm because the maximum in the spectra is at ~1550 1/cm. We expect greater accuracy in the purity index as a result. The results are summarized in Table 2 for the 10 repeated measurements of XP24-001 GJ. Regarding the values (average, minimum, maximum) in Table 1, minimal changes occurred in the third decimal place.

Table 2 :- Measured ATR-FTIR spectra (400 to 1600 1/cm) and their Purity index P with the reference spectra XP 24-001 GJ Std (with normalisation at maximum intensity, no smoothing, threshold = 0.95)

Code of the spectra XP 24-001 GJ Std.	**Purity index** Reference	**Slope**	**Intercept**
XP-24-001-GJ-Sample 1			
XP-24-001-GJ-Sample 2	0,9996	1,0111	-0,0009
XP-24-001-GJ-Sample 3	0,9996	1,0322	0,0000
XP-24-001-GJ-Sample 4	0,9992	1,0168	-0,0016
XP-24-001-GJ-Sample 5	0,9992	1,0057	-0,0010
XP-24-001-GJ-Sample 6	0,9971	1,0120	0,0019
XP-24-001-GJ-Sample 7	0,9980	1,0215	0,0026
XP-24-001-GJ-Sample 8	0,9975	0,9930	0,0120
XP-24-001-GJ-Sample 9	0,9994	1,0267	-0,0003
XP-24-001-GJ-Sample 10	0,9978	1,0197	0,0021
Average	0,9986	1,0154	0,0016
Minimum	0,9971	0,9930	-0,0016
Maximum	0,9996	1,0322	0,0120

3.2 ATR-FTIR Measurement of a Powdery Mixture with 10 Additives with Impurities;

3.2.1 Entire range of wave numbers;

In a 2nd step we added 5% „impurities“ to 95% of XP24-001 GJ; Table 3. The results are very surprisingly. Beside XP-24-001-GJ-MH the purity indices are all >0.99. Only the sample with magnesium hydroxide shows a purity index of 0.969 which is higher than the reality. This approach to QC seems to be rather inappropriate.

Table 3 :- Measured ATR-FTIR spectra (400 to 4000 1/cm) and their Purity index P with the reference spectra XP 24-001 GJ Std (with normalisation at maximum intensity, no smoothing)

Code of the spectra	**95% XP24-001 GJ + 5% of**	**Purity index**	**Slope**	**Intercept**
XP 24-001 GJ Std.		Reference		
XP-24-001-GJ-AC316	AC316	0,997	0,986	0,000
XP-24-001-GJ-Caacac	Caacac	0,994	0,941	0,002

Code of the spectra	95% XP24-001 GJ + 5% of	Purity index	Slope	Intercept
XP-24-001-GJ-CaSt	Calcium stearate	0,991	0,902	-0,005
XP-24-001-GJ-MH	Magnesium hydroxide	0,952	0,860	0,006
XP-24-001-GJ-PE	Polyethylene wax	0,999	0,975	0,004
XP-24-001-GJ-Penta	Pentaerytrithol	0,995	0,982	0,002
XP-24-001-GJ-THEIC	THEIC	0,999	0,987	0,001
XP-24-001-GJ-Zeolite	4A Zeolite	0,989	0,928	0,000
XP-24-001-GJ-ZnSt	Zinc stearate	0,999	1,045	0,004
Average		0,991	0,956	0,002

3.2.2 Fingerprint range of wave numbers;

We applied as the same procedure as described in section 3.1.2 for the mixtures with 5% „impurties“. The results are summarised in table 4. Even in fingerprint range ATR-FTIR seems not to be a useful tool for QC of powdery PVC stabilisers.

Table 4:- Measured ATR-FTIR spectra (400 to 1600 1/cm) and their Purity index P with the reference spectra XP 24-001 GJ Std (with normalisation at maximum intensity, no smoothing)

Code of the spectra	95% XP24-001 GJ + 5% of	Purity index	Slope	Intercept
XP 24-001 GJ Std.		Reference		
XP-24-001-GJ-AC316	AC316	0,996	0,981	-0,002
XP-24-001-GJ-Caacac	Caacac	0,992	0,955	-0,005
XP-24-001-GJ-CaSt	Calcium stearate	0,984	0,907	-0,009
XP-24-001-GJ-MH	Magnesium hydroxide	0,968	0,933	-0,003
XP-24-001-GJ-PE	Polyethylene wax	0,999	0,985	-0,001
XP-24-001-GJ-Penta	Pentaerytrithol	0,989	0,978	-0,004
XP-24-001-GJ-THEIC	THEIC	0,998	0,987	-0,002
XP-24-001-GJ-Zeolite	4A Zeolite	0,977	0,929	-0,005
XP-24-001-GJ-ZnSt	Zinc stearate	0,998	1,030	0,003
Average		0,989	0,965	-0,003

3.3 Comparison of ATR-FTIR of some pure raw materials;

One reason why ATR-FTIR spectroscopy is not very suitable for QC of complex, powdery PVC stabilisers is that various ingredients such as metal hydroxide, metal oxides, zeolites, hydrotalcites... are inorganic in nature. On the other hand, the spectra of some raw materials should only differ minimally. Furthermore, other raw materials such as ß-diketones, tinting pigments, antioxidants, etc. are only present in the mixture in very small doses.

For example, the spectra of non-polar and oxidized PE wax should only differ slightly. Non-polar PE wax is oxidized and contains peroxy, hydroxy, carbonyl and carboxyl groups, and only to a relatively small extent. We have therefore superimposed both spectra of these raw materials in Figure 4 and calculated the purity index.

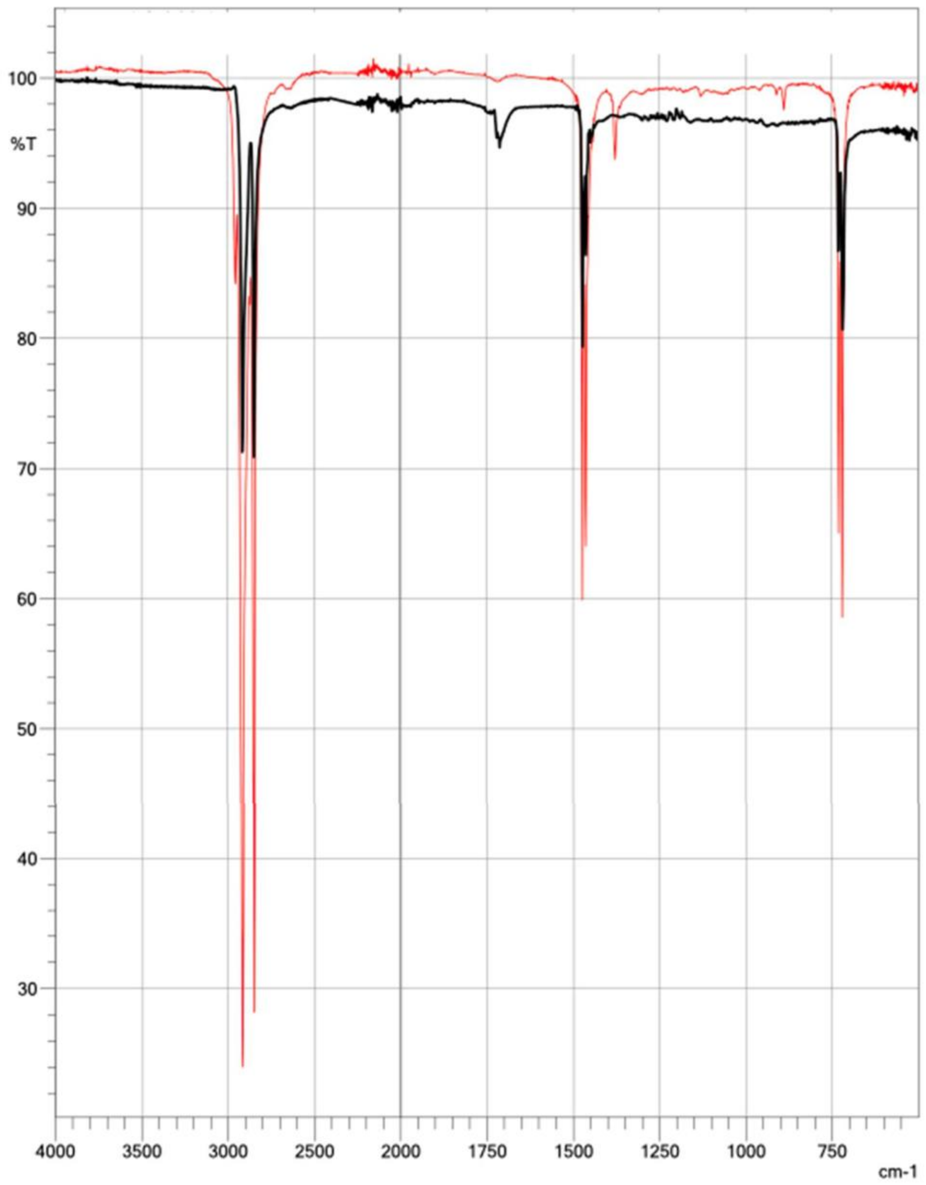

Figure 4:- Overlay of spectra PE wax (read) and AC316 (black)

For the entire range of wavenumbers, the purity index is 0.8077. The slope of the correlation line, which intersects the y-axis at about 0, is 0.7163. As expected, AC316 contains about 80% PE wax.

In the fingerprint area, the values change only slightly. The purity index is 0.7751, the slope of the correlation line is significantly steeper at 0.9080. The intersection with the y-axis is still at approximately 0.

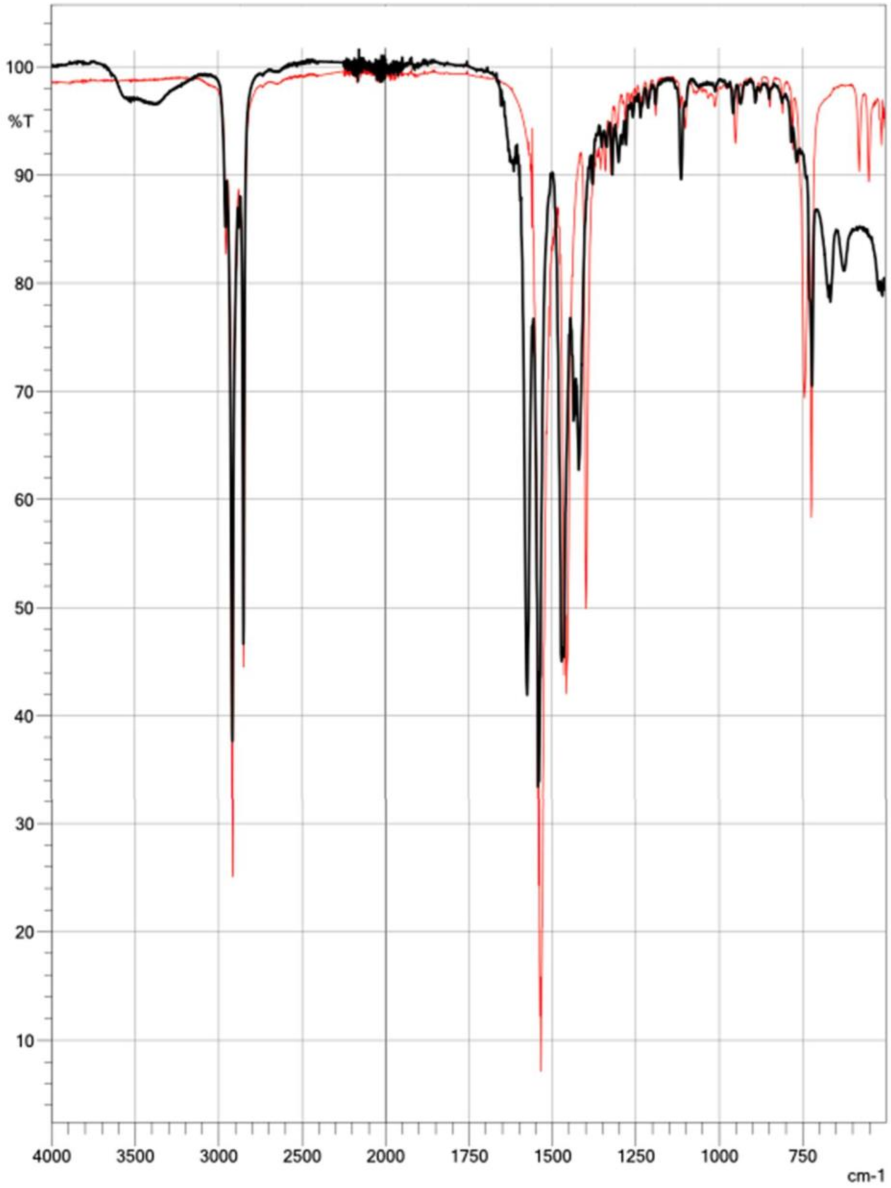

Figure 5:- Overlay of zinc stearate (read) and calcium stearate (black)

We expected only minimal differences for the FTIR spectra of calcium and zinc stearate; Figure 5. Surprisingly, both spectra differ significantly. Although these are pure substances, the purity index of zinc stearate is 0.5440 (entire range of wave numbers) and 0.3685 (fingerprint range). In both cases, the slope of the correlation line is approximately 0.36 and 0.39, respectively. The line intersects the y-axis at approximately 0.

Based on these two examples alone, it is impossible to determine the "purity" of powdery multicomponent mixtures with sufficient accuracy. In addition, calcium and zinc stearate or non-polar and oxidized PE wax have very different, sometimes opposing, effects in PVC processing.

3.4 Tests of the PVC Stabilisers in Application lab;

However, we expected a wider range in the purity indices of a mixture with 5% „impurities“ which will have a huge influence on the processing and the properties of a PVC product. That's why we investigated the performance of the 10 stabiliser samples in application lab in a typical Indian pipe dryblend with

100.0 phr S-PVC
10.0 phr uncoated calcium carbonate
0.4 phr AC617
2.7 phr stabiliser

At a dosage of 2.7 phr, the stabiliser will contain 2.565 phr XP 24-001 GJ Std and 0.135 phr „impurity“. We expected following influence on processing and final performance on the product:

- AC 316 will reduce the fusion time and increase the maximum torque on torque rheometer. During product with twin screw extruder it will increase the extrusion torque, slightly the extrusion pressure and the melt temperature [1]
- Calcium stearate (CaSt) will mainly accelerate the fusion time [1]. It might have a small influence on initial colour and stability [1]. Slightly because of the low dosage. It well have no or minor effects on extrusion.
- Caacac is accelerating the fusion time too but it will also increase the maximum torque on rheometer, the extrusion torque and the melt temperature while the melt pressure drops. Even at this low dosage it will improve the stability and the initial colour [1]
- Magnesium hydroxide (MH) is expected to have no significant influence on rheology at this low dosage. Because of its function as an acid scavenger it improves the stability [1].
- Regarding rheology we await for zeolite as the same as for magnesium hydroxide but the stabilising mechanism is different. It acts as an anion exchanger replacing two sodium ions on its surface by one zinc cation [1].
- Pentaerytrithol (Penta) and THEIC are considered as polyols [1]. They improve stability but they don't really affect rheology.
- Neutral PE waxes are rheological additives which don't touch stability and colour. However, they delay fusion and reduce the maximum torque on rheometer, the extrusion torque, melt pressure and temperature [1]. How strong this influence is will depend on the brand of PE wax.
- Zinc stearate (ZnSt) acts as both a lubricant, color improver and acid scavenger, whereby the zinc chloride formed catalyzes the decomposition of the PVC in the PVC. Therefore, we expect a delay in the fusion time and a reduction in the maximum torque on the rheometer, lower torque, lower melt pressure and a lower melt temperature during extrusion, a better initial color and less stability.

However, related to the dosage these expectations might not be visible in all cases due to the low dosage. We produced the PVC dry blends in a hot mixer, tested them with a torque rheometer on the next day, extruded them with a single-screw extruder and measured the color values and stability of the extruded strips in the oven test; Table 3 and Figure 6. Furthermore, we calculated the extrusion torque by using the equations in [19].

Table 3:- Result in application lab from torque rheometer, calculated extrusion torque and colour values; Dryblend composition 100 phr PVC, 10 phr uncoated calcium carbonate, 0.4 phr PE wax type AC617, 2.7 phr stabiliser; preparation as described in 2.2)

„Impurity“	-	AC 316	Caacac	CaSt	MH	PE wax	Penta	THEIC	Zeolite	ZnSt
Rheometer results										
Fusion time (sec)	138	119	93	132	169	212	125	172	163	219
Max. Torque (Nm)	26,8	30,0	30,0	26,6	26,5	24,0	27,1	25,9	25	24,7
Temp. at Maximum Torque (°C)	179	179,6	178,3	180,1	180,4	181	180,3	180,9	182,1	180,8
End Torque (Nm)	25,2	27,4	26,8	25,5	25	23,4	25,6	24,3	24,8	24,1
Temp. at End Torque (°C)	185,6	187,8	187,1	186,1	185,7	184,5	186,3	185,5	185,6	184,7
Calculated extrusion torque (%)	70,0	76,4	73,0	72,8	68,2	65,9	71,4	64,1	74,4	68,8
Colour values										
L*	63,5	63,2	67,2	65,7	68,2	64,4	64,6	64,6	66,2	66,4
a*	1,4	2,1	0,5	0,7	0,3	0,5	0,6	0,6	0,5	0,6
b*	11,2	11,4	5,9	8,9	9,0	9,0	11,0	8,7	9,3	8,9

Interestingly, not all of our expected predictions have come true.

- With reference to fusion time: AC 136, Caacac, CaSt, ZnSt, PE wax and Penta matched with our expectations inside the experimental error but not MH, THEIC and Zeolite. They should have no influence on rheology. In the case of MH it can be explained with it's reaction with free stearic acid inside the dryblend.
- In tendency as the same is valid for the maximum torque on rheometer and
- The calculated extrusion torque
- Regarding stability we found more or less our expectations confirmed. Only the PE wax in trial 6 is an exception. At the time being we do not have any explanation for this.

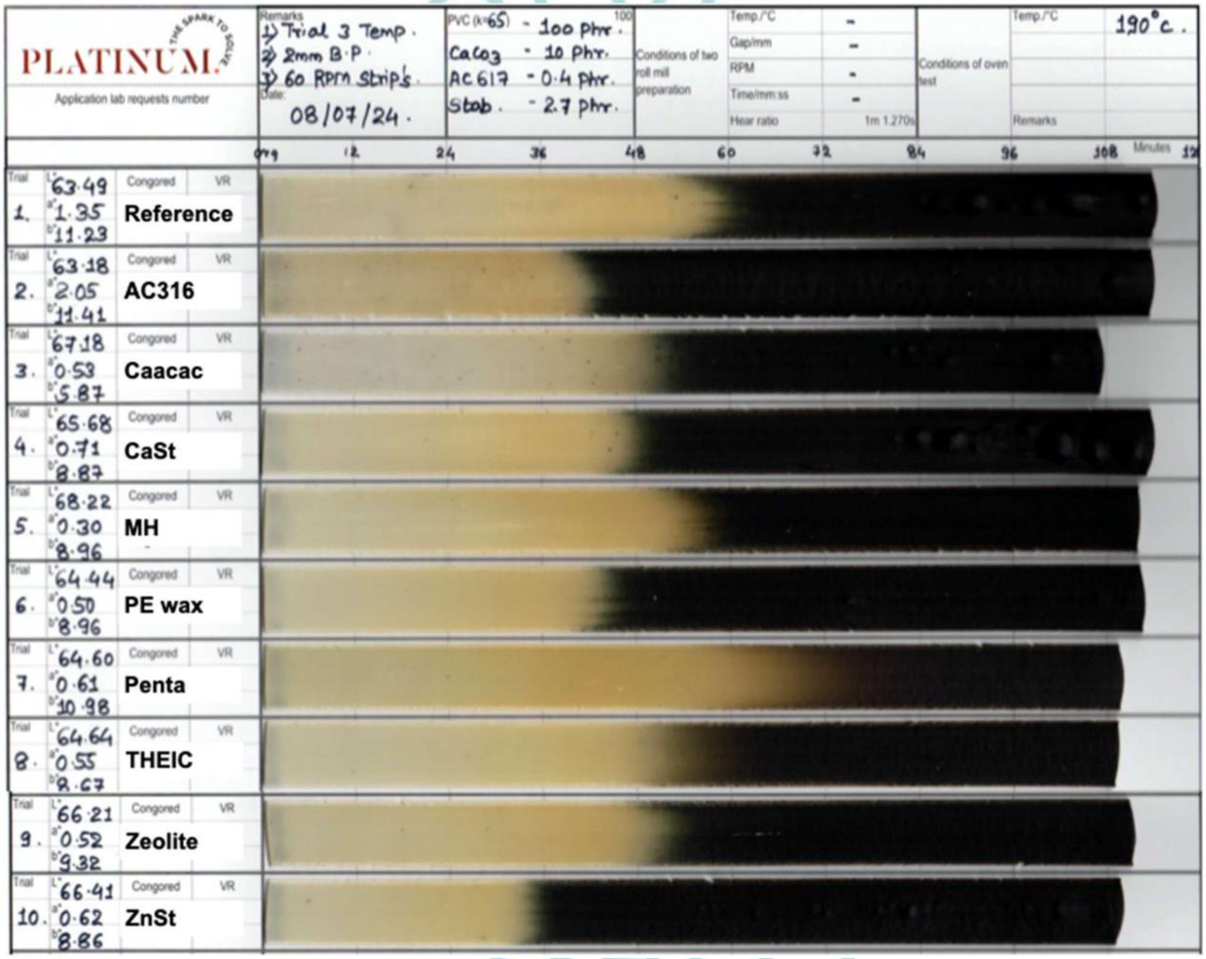

Figure 6:- Oven test results

3.5 ATR-FTIR of commercially available PVC Stabilisers and industrial trials;

So far we have focused on correlation and testing in the application laboratory. In the following section we compare two commercially available PVC stabilisers for the same customer, the same application and the same pipe dimensions. In Figure 7 the overlays are shown in the entire IR spectral range and in Figure 8 in the fingerprint range.

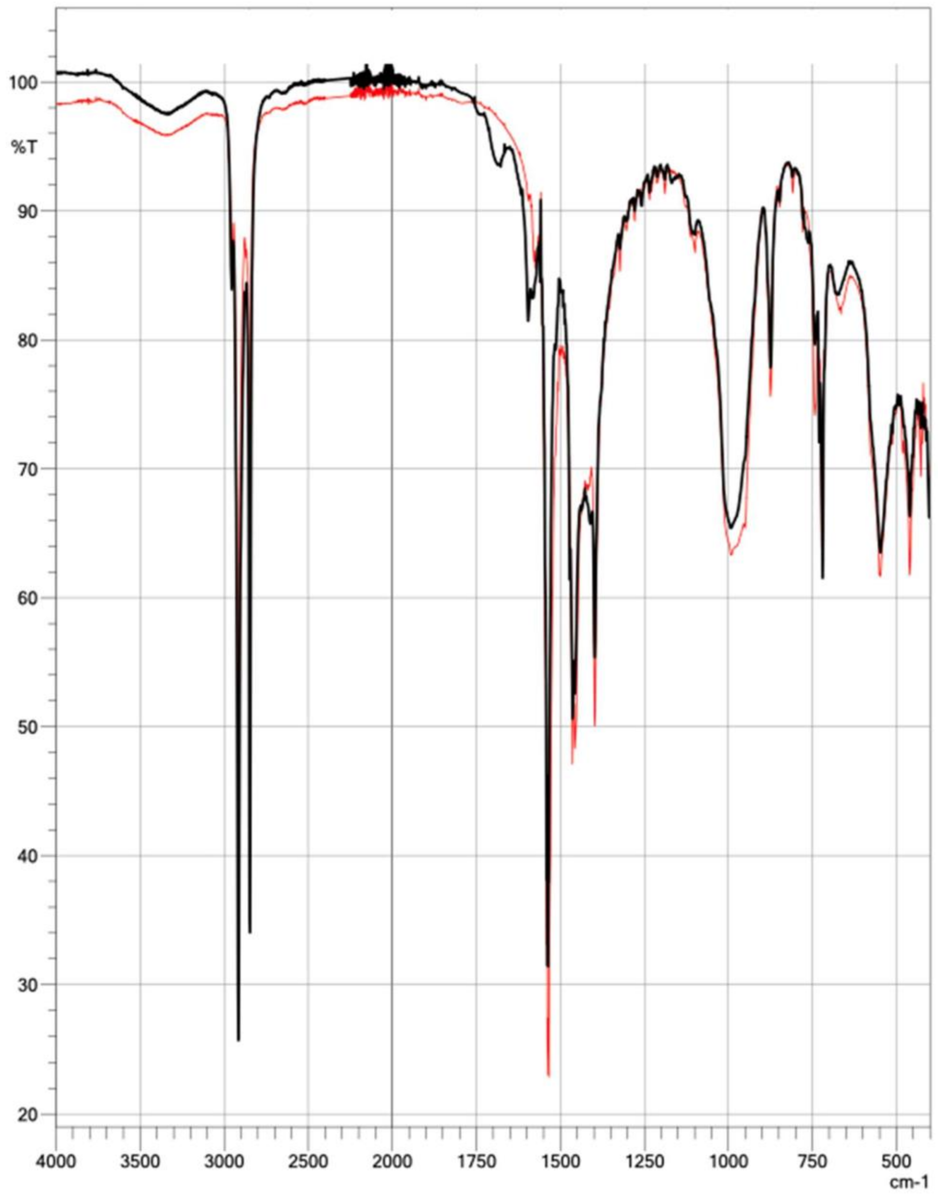

Figure 7 :- FTIR overlay of stabilisers A (read) and B (black) (full spectral range; normalised, purity index: 0.9302, slope: 0.9077, intercept: 0.0012)

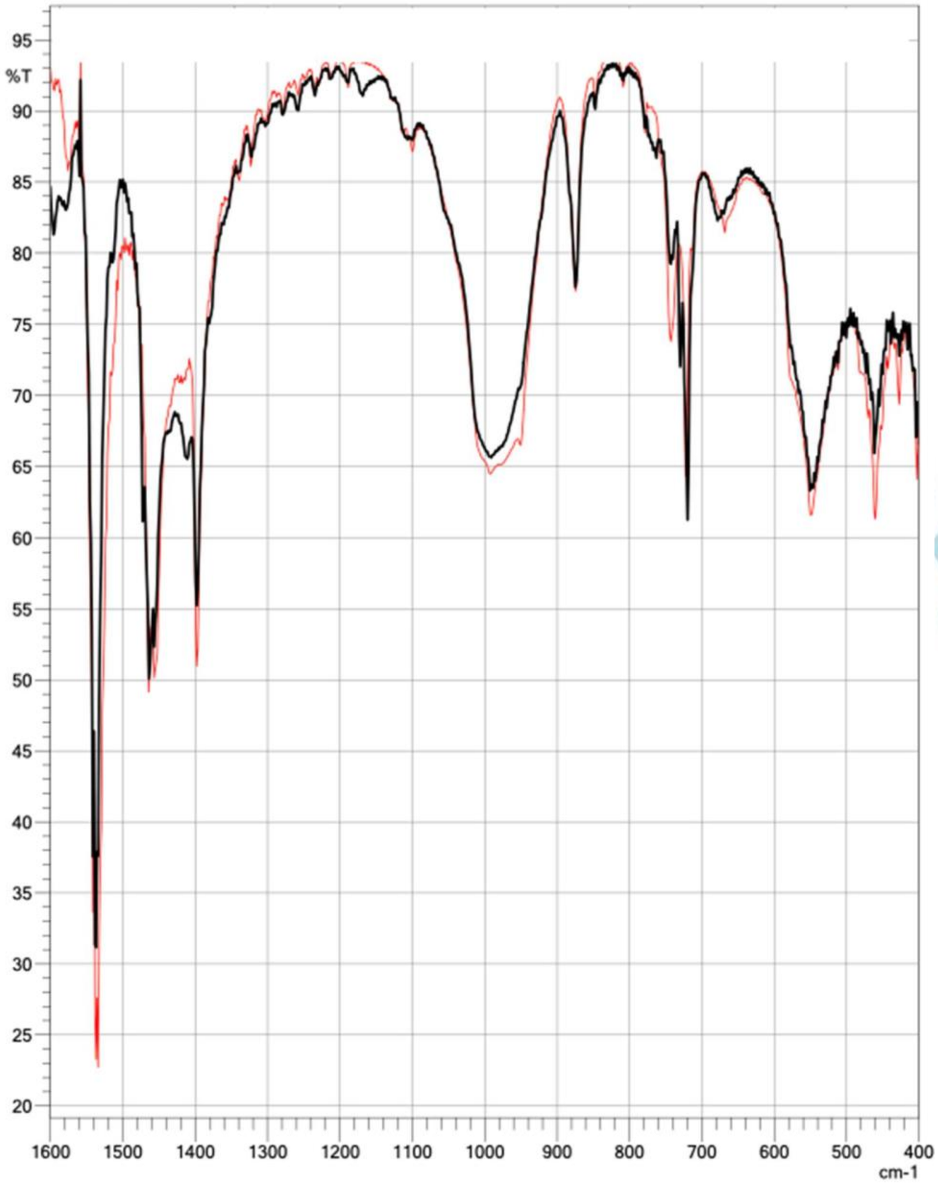

Figure 8:- FTIR overlay of stabilisers A (read) and B (black) (fingerprint range; normalised, purity index: 0.9269, slope: 0.9269, intercept: -0.0083)

Visually, the two stabilisers differ only slightly, but in terms of purity index they only agree by 93%. If we relied on this information, we should expect very different performance during extrusion. The results are summarized in Table 4 in extrusion industrial trial.

Dryblend composition:

- 100.0 phr S-PVC
- phr uncoated filler (not disclosed)
- 3.6 phr stabiliser
- phr pigment masterbatch (not disclosed)
- 0.3 phr wax (type not discolosed)

Table 4:- extrusion industrial trial

Extruder: Kabra KET 92/28	Application: pipe, 2 inchs, double strand die	
	Extruder setup Main screws: 39 rpm Feeder screw: 70 rpm BZ 1: 175/175°C BZ 2: 175/175°C BZ 3: 165/165°C BZ 4: 165/165°C BZ 5: 160/160°C Adapter: 168/168°C	
	DZ 1: 168/168 DZ 2: 170/170 DZ 3: 170/170 DZ 4: 175/175 DZ 5: 190/190 DZ 6: 192/192 LHT 1: 165/165 SOF: 165/165	DZ 1: 168/168 DZ 2: 170/170 DZ 3: 170/170 DZ 4: 175/175 DZ 5: 190/190 DZ 6: 192/192 LHT 1: 165/165 SOF: 165/165
Haul off: 3.90 m/min		
Stabiliser	A	B
Torque/Load (A)	87	86
Melt pressure (bar)	310	300
Melt temperature (°C)	173	173
Output (kg/hr)	650	650
Color	OK	OK
Surface (inside/outside)	OK/OK	acceptable/acceptable

Industrial tests have shown that the same extrusion behavior and product properties can be achieved, although the FTIR spectra only agree by 93% because the compositions of the stabilisers are different.

4. Conclusion;

Solid PVC stabilisers based on calcium and zinc are multi-component mixtures. We have tested whether ATR-FTIR spectroscopy is a suitable method for quality control. We added 5% of the respective additives to 95% of a known mixture and in no case did we find a purity of less than 95%. This is because various additives have very similar spectra, such as calcium and zinc stearate or HDPE wax and oxidized HDPE wax, all four of which have a very strong influence on the processing behavior of PVC in industrial production. This was proven by tests on a laboratory scale. Furthermore, we have proven that two PVC stabilisers with different compositions have the same processing behavior on a production extruder and the same properties of the finished product, although they only match 93% in the ATR-FTIR spectrum. We therefore come to the conclusion that ATR-FTIR spectroscopy is only very conditionally a suitable method in the PVC industry for quality control of solid stabilisers.

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