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“Evaluation of the effects of DCOIT biocide on a liquid Ca/Zn stabiliser for PVC flooring, optimization of the technology”

Experimental degree thesis

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Abstract

In this scientific work has been evaluated the interaction between the DCOIT fungicide and a liquid Ca/Zn stabiliser for PVC flooring. In particular the liquid stabiliser underwent yellowing issues when came in contact with the fungicide preventing the material from its transparency. Through spectrophotometric and colorimetric tests was clear that the main responsible of the yellowing was the phosphite, an important component of the Ca/Zn stabiliser, which chemically reacted with the biocide leading to the breakage of its isothiazolynic ring. An innovative work on the liquid stabiliser was performed in order to find out a composition which could keep together the DCOIT and the phosphite with no problems of yellowing to the stabiliser. 3 alternative phosphites were tested but all three gave to the top coat formulation an acceptable yellowing (some more some less) for PVC flooring applications. For this reason was modified the composition of the Ca/Zn stabiliser in particular was modified the soap regulating the metal ratio and was eliminated the phosphite in order to avoid the reaction with the fungicide. In parallel innovative Ba/Zn stabilisers were prepared, those with an high level of Ba and low level of phosphite gave good results in terms of ageing tests and static thermostability tests which were used in order to simulate the integrity of the compositions in different real conditions for example the carpet covering on the PVC floor. All the chemical analysis and probes on the stabilisers and their optimized formulations were performed in the R&D laboratory of Reagens S.P.A

INTRODUCTION (1)

PVC (1.1)

PVC is one of the most important thermoplastic polymers worldwide (next to PET and PP), it's a naturally white and brittle plastic insoluble in alcohol and slightly soluble in THF. PVC is produced generally in two forms: a rigid or unplasticized polymer and the second as a flexible plastic. In its base form PVC is characterized by its rigid yet brittle structure, plasticizers are generally introduced in order to make softer and more flexible PVC which is commonly used in construction as insulation on electrical wires or in flooring for homes, hospitals schools, and other zones in which a sterile environment is needed. Conversely rigid PVC end uses are mostly pipes for plumbing and siding in the field of construction. Some of the most relevant characteristics of PVC are: higher density compared to most plastics, low costs of production, high durability and strength due to rigidity.

PVC is a typical thermoplastic polymer. It offers a a wide variety applications and advantages across multiple industries in both its rigid and flexible forms. Tipically Rigid PVC has a high density for plastic making it extremely hard and strong. The fact that it is readily available and economical respect other plastics makes it an easy choice for many industrial applications, in addition its high chlorine content makes the material fire resistant another reason why PVC has gained such popularity across various industries. Most important drawbacks of PVC are the scarse heat capacity and the presence of toxic fumes emitted when PVC is melted or subjected to fire.

PVC production

PVC can be made from emulsion (12%), suspension (80%) or bulk (8%) polymerization [1].With PVC obtained from suspension (S-PVC) the monomer is introduced in the polymerization reactor, through high speed agitation small drops of polymer rapidly forms. In particular drops of VCM (vynyl chloride) transforms in PVC when a soluble catalyst is introduced in a high pressure reactor in the range of 40-60°C. At the end of the process the not reacted monomer is removed together with the water and solid undergoes essication. PVC final product appears like a white resin not toxic and with no fragrance. In emulsion process (E-PVC) surfactants (soaps) are used to disperse the monomer in water. Soap micelles trap inside the monomer and polymerization takes place using water soluble initiators. The process can be either continuous or batch but both lead to a polymer latex which is very fine, excess of monomer is recovered and polymer particles are dried at the end. In mass, (M-PVC) water, emulsifying agents and protective colloids are absent, the polymer is insoluble in the monomer and precipitates down to form grains that have no tendency to agglomerate. In the first stage the monomer is agitated and a pre-polymer is formed, then it is transferred in an autoclave where the process stops when 70-90% of the monomer has been converted.

Health concerns of PVC, Vinyl Plus and sustainable approach (1.2)

It's widely thought that harmful by-products are created as a result of the chemical composition of PVC, during both the creation and decomposition of the product [2]. Countries as well as some brands that are based around social and corporate responsibilities have taken steps to limit the creation of PVC, or even ban it altogether so as to avoid these health concerns. Moving PVC industry to a low carbon circular economy is a priority of the European PVC compartment. PVC is an intrinsically low-carbon plastic: 57% of its molecular weight is chlorine derived from common salt; 5% is hydrogen; and 38% is carbon [3].It is an extremely durable and cost-efficient material which can be recycled several times at end of life without loosing its essential properties.

Several PVC applications – such as pipes, window profiles, cables, flooring, membranes and films – have been analysed in terms of Life Cycle Assessments and eco-efficiency, and they have shown excellent environmental performance.

Thanks to their intrinsic characteristics and properties, PVC products can make positive contributions towards several of the UN Sustainable Development Goals' (SDGs) targets. To help eradicate poverty, PVC can provide goods and services that underpin basic human needs, making them available for all, at affordable costs.

PVC pipes help provide access to clean water and sanitation all over the world. PVC piping systems are easy to install and highly durable, enabling efficient irrigation even in remote areas and addressing global issues such as soil erosion and water scarcity.

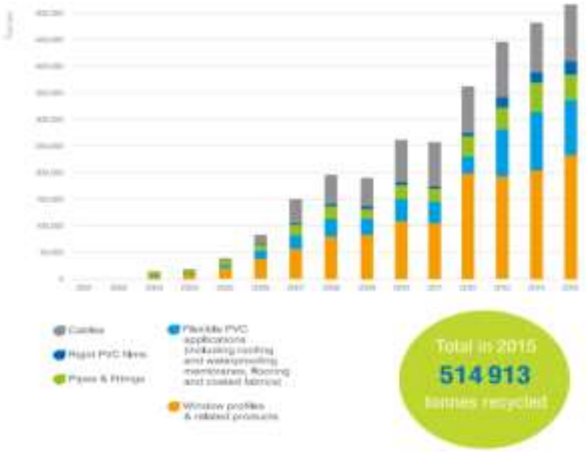
In healthcare, PVC devices account for about 40% of all plastics-based medical devices in hospitals, where they are used for their durability, barrier properties and physiological inertness. Healthcare buildings benefit from PVC applications such as flooring, wall coverings and window profiles in terms of safety and hygiene as well as personal comfort. PVC is also utilised for temporary emergency structures (field hospitals, tents to protect against biological risk and medical devices) that are suitable for health emergencies.

In the building and construction sector, which accounts for around 70% of PVC volumes, the main PVC applications such as windows profiles, pipes, flooring, roofing membranes, wire and cable offer solutions that are efficient in terms of cost, energy, and resources.

PVC products not only save energy during use, but they are also integral to renewable energy technologies. Examples include transparent pipes for photo-bioreactors, photovoltaic cells on reflective PVC roofing membranes, wind turbine blades pressure pipes for geothermal projects, pipes in biogas plants and solar pond liners.

Vinyl Plus is the European PVC industry'scommitment to sustainable development, whose aim is to improve the sustainability performance of this thermoplastic material. Mainly Vinyl Plus works to improve the recycling rate of PVC to decrease its environmental criticisms and address climate change. The theme of the most recent Vinyl Sustainability Forum "More Vinyl, Less Carbon" summarises the challenges of the PVC sector for the next decade, companies have to re-think and re-design their products in order to decrease raw materials and energy expenses, increase the life cycle and the recycle of their products as much as possible.

Compared with PP and PS, PVC is characterized by a low consumption of primary energy use in the manufacture phase this is the most important benefit of PVC but anyway it has a carbon footprint and an environmental impact as any human material in the world. Vinyl Plus initiative as to reduce GHG emissions along the entire production process, implementing the use of renewable energy and techniques in order to increase the efficiency and the life chain of any material used. In 2020 energy global energy consumption in the PVC compartment has decreased of 20% respect 2019, this thanks to the adoption of a new methodology called "EPD Plus" to evaluate the toxicity and the environmental risks of PVC stabilisers and to develop synthetic ways to produce PVC resins from Bio Ethylene from biomasses. Furthermore PVC is a recyclable material, it has the longest story of recycling of all plastics in the world, mechanical recycling systems are advanced and large volumes of PVC to be recovered are available. Avoiding the scrap of PVC at the end of life permits to reduce landfill requirements, then the thermoplastic nature of PVC allows to recycle PVC several times without significant losses of performances. Windows, building products and cables are the most recycled PVC products (rigid PVC recycling is more difficult) as can be seen in the **Graph 1** in the period 2010-2015 the total PVC recovered doubled up.



Graph 1: increase of the PVC recycling rate in the period 2001-2015

Vinyl Plus target of 800.000 tonnes set in (2015-2020) of PVC per year corresponding to 40 % of PVC wastes globally, this is not an easy goal to be achieved but it could be favoured by the fact that PVC recycling has become an economical business that guarantees profits to the entire compartment. Using recycled PVC helps meet resource-efficiency targets thus allowing the preservation of the natural resources. Has been calculated [3] that recycling guarantees up to 92% of CO_2 savings and primary energy use consumed to develop the recovery process is half respect virgin PVC production, obviously depending on the PVC type.

Thermal degradation of PVC (1.3)

PVC is technically a stable material not so prone to be thermally degraded. Most of degradation processes happens in low oxygen concentrations. Thermal degradation is a process without oxygen. It has been extensively studied because, even if PVC does not contain oxygen, some defects are the main responsible of the strong lack of thermal stability. Chlorines bonded to tertiary carbons and allylic chlorines are the weak points for thermal stability [4], Fig 1.

Fig 1: Degradation of an allylic chlorine systems

From defects a “cage reaction” called zip-elimination [5], leads to the formation of polyene sequences with the release of HCl and finally to SECONDARY REACTIONS:

- Crosslinking of the PVC matrix (Intermolecular Diels Alder reaction and Friedel-Craft alkylations)
- Benzene emissions due to intramolecular reactions of CIS TRANS sequances.

An example of intramolecular cyclization is reported in Fig 2

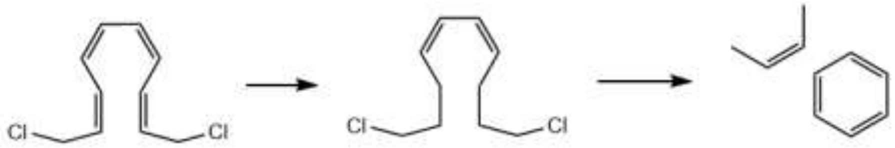


Fig 2: release of Benzene after intramolezular cyclization

Thermal degradation causes a strong changes of color and viscosity in the polymer, leading to an increase of the temperature during the process.

Mechanism of thermal degradation has been object of debate since the discover of PVC, generally the most important pathways of degradation are radical, six center concerted, ion pair or quasi ionic and HCl and Lewis acid mediated way.

Radical mechanism

The most important hypothesized radical route [4] sees the formation of a macroradical followed by a Beta elimination of Cl and formation of a polyenic sequence. Double bond formation is favored by the high acidity of the methylenic Hydrogen, Fig 3.

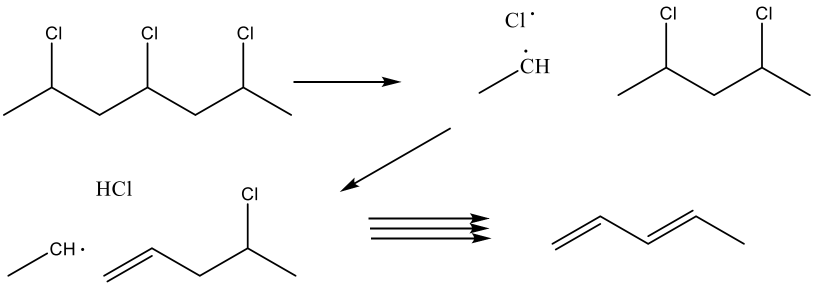


Fig 3: Radical mechanism of thermal degradation of PVC

Six center mechanism

Starnes in 1980 thought that a 6 members mechanism could be possible for the thermal degradation of PVC, Fig 4.

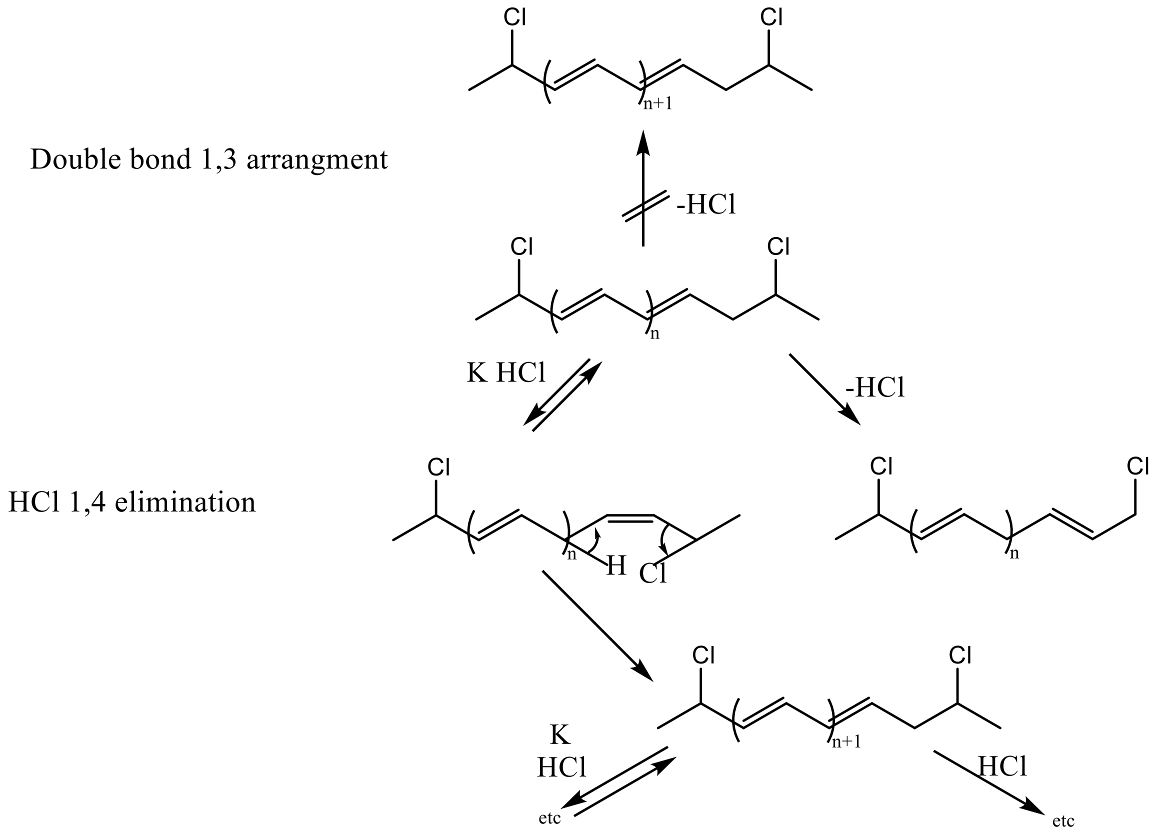


Fig 4: Six center concerted mechanism of thermal degradation of PVC

Usually Starnes mechanism is considered more probable respect the radical, because it takes into account the role of HCl as catalyst of the degradation. There are “n” sequences of polyens available for the degradation, the trans position leads to a rearrangment to a stable 6 members ring which is stable thermodinamically. After the chlorine rearrangment a 1,4 elimination takes place. The elimination weakens the adjacent position so is possible to define this HCl catalyzed mechanism as selective taking in consideration the dynamic of a zip elimination.

Starnes used two molecules to understand the mechanism of reaction. The first, trans-9-chloro-6-tridecene, was unreactive because the chlorine is not allylic so the double bond did not display any rearrangment, Fig 5.

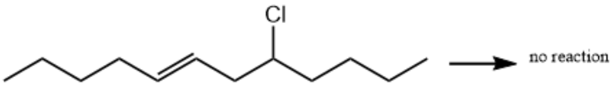


Fig 5: not allylic chlorine doesn’t undergo rearrangment

Second molecule gives 1,2 elimination [6] (Fig 6) 1,4 elimination in fact doesn’t take place (Fig 7)

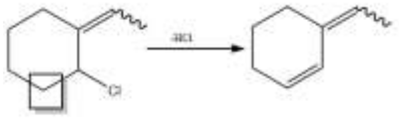


Fig 6: 1,2 elimination

Fig 7: 1,4 elimination

Ionic mechanism

Ionic mechanism consists of a two parts, the first is a “ion pair” mechanism while the second a “free ion” mechanism. Reaction takes place in a medium without solvent, the chloride attacks a methylenic hydrogen and a double bond forms consequently to the releasing of HCl. This creates a weak adjacent position yielding another double bond through the same mechanism, this route gives maximal 14-20 polyene sequences and after it stops, Fig 8.

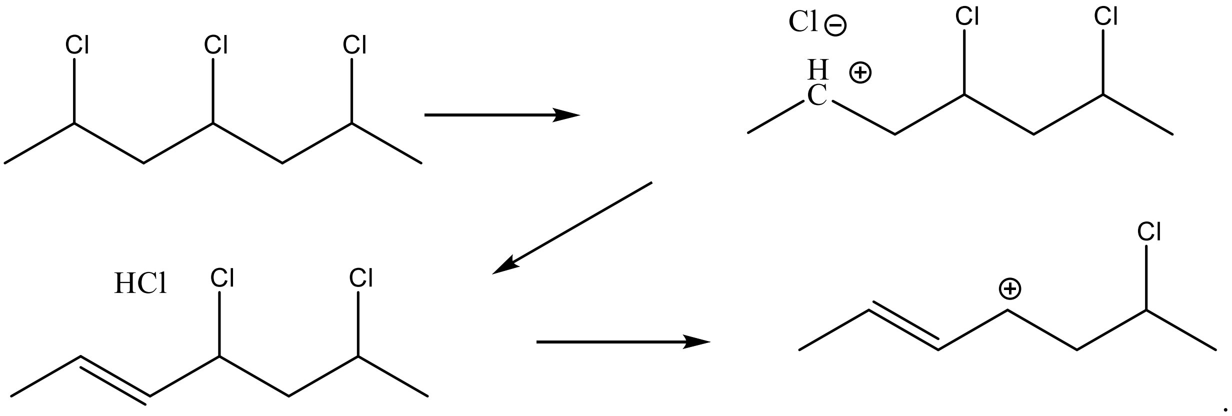


Fig 18 : Ion pair mechanism PVC degradation

Carbocation permits the delocalization of positive charge, HCl acts as auto-catalyst, the mechanism is reported in Fig 9.

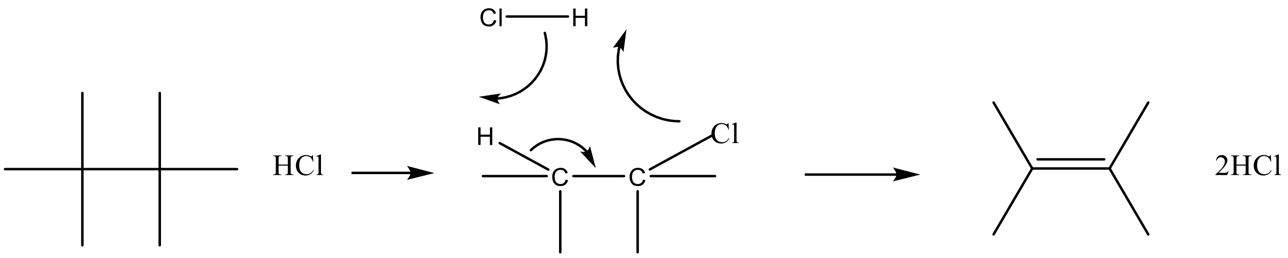


Fig 9: catalytic activity of HCl

Considerations that seem to confirm the ion pair mechanism are the following:

- In polar solvents the HCl elimination speeds up
- Zip elimination is selective because each elimination weakens the adjacent position
- HCl exploits its Lewis Acid catalytic activity

All Lewis Acids catalyze PVC degradation [7], in particular $ZnCl_2$ presence can be useful for flame retardance and smoke suppressant. $ZnCl_2$ promotes the zip elimination and stimulates the crosslinking of polyene sequences forming in a stereospecific way trans sequences.

Stabilization and PVC stabilisers (1.4)

PVC in order to be processed in articles must be stabilized. Stabilizers serve to protect the PVC during the transportation and to give to the hand work large life. Stabilization is a way to slow down the zip elimination quenching the release of HCl, avoiding the increase of viscosity and temperature stopping the creation of polyene sequences and their crosslinking. Factors such as process technology involved, technical requirements of PVC and product, regulatory requirements and cost, influence the choice of the stabilizer utilized. Stabilisers can be solid or liquid.

Liquid mixed metal stabilisers

The liquid mixed metal stabilizers are used in several PVC flexible applications [8] like: calendered films; extruded profiles; injection moulded, soles, footwear; extruded hoses and plastisols (flooring, wall covering, artificial leather, coated fabrics, toys). Liquid mixed metal stabilizer systems are based on Ba, Zn, Ca, Mg or K carboxylates. In general liquid mixed metals like Ba-Zn, Ca-Zn and Mg-Zn require the addition of co-stabilisers, antioxidants and organo-phosphites to provide optimum performance. The costabilizers are usually imparted to the liquid mixed metal stabilizer system. To adjust the viscosity different solvents are used including hydrocarbon solvents and plasticisers.

Liquid Ba-Zn stabilizers and liquid Ca-Zn stabilizers have successfully replaced cadmium-based stabilizers in any PVC semi-rigid and flexible applications. The stabilizers are formulated to meet specific requirements such as good initial colour, long-term stability, good transparency, good printability, weatherability, ageing resistance, good compatibility with all types of PVC, with fillers, and pigments. A good stabilizer achieves the best possible compromise of all the necessary requirements, including cost.

In the late 1930s it was discovered that Group IIA metal soaps (Mg, Ca ,Sr and Ba) guarantee to the PVC excellent long-term thermal stability but they caused a strong PVC discoloration to yellow. Oppositely group IIB metal soaps (i.e Zn and Cd) gave a wonderful initial color, but the thermal degradation of PVC occurred quickly and catastrophic after few minutes Cd and Zn soaps act as primary stabilizers displacing the allylic chlorine and Mg, Ca, Sr and Ba act as co-stabilizers.

Calcium zinc stabilizers

Calcium based stabilisers (including Ca-Zn) are now largely used in wires and cables, in window and technical profiles (also foamed ones), and in any type of pipes (such as soil and sewer pipes, foam core pipes, corrugated pipes and cable ducting) as well as the corresponding fittings. Calcium based stabilisers have also been introduced in PVC rigid calendering film production when improved organoleptics characteristics are required, for instance as alternative to tin carboxylates in PVC blown film shrinkable and for candy wrap.

Barium Zinc

The majority of stabilisers in this group are liquid, mixed metal soaps which have similarities to some calcium/zinc stabilisers described earlier and are generally used in the form of a carboxylate. However, solid forms are also manufactured which are used to provide specific properties.

As in the case of calcium/zinc heat stabilisers, all these products require the addition of co-stabilisers to provide optimum performance. These are the same types of products as are used with calcium/zinc stabilisers. Solvents are also sometimes incorporated. Generally Ba/Zn stabilisers are more powerful than Ca/Zn [] and are characterized by a lower title of Zn. As documented in the literature [10], PVC stabilizers could be classified based on mode of action into the following.

Primary stabilizers

These types of stabilizers function by reacting with allylic chlorine atoms, the intermediates in the zipper degradation chain, thereby preventing further dehydrochlorination (Fig.10).

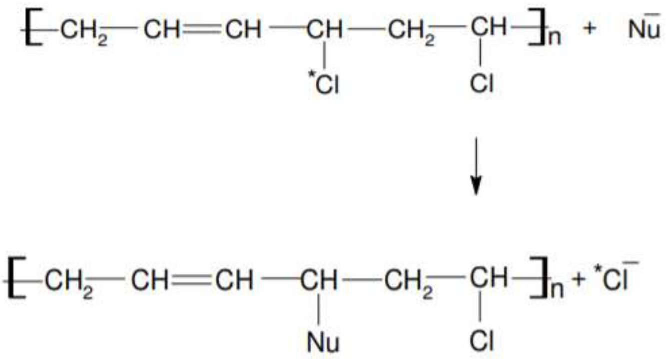


Fig 10: Primary stabilizers mechanism

This process should be faster than the chain propagation itself, requiring a very active nucleophile. However, the reactivity of the nucleophile should not be so high as to react with the secondary chlorine of the PVC chain, a process that rapidly exhausts the stabilizer. To be effective, the stabilizer must be associated by complex formation with the polymer chlorine atoms, which means it should have a Lewis acid character.

Secondary stabilizers

This type of stabilizers function by scavenging the HCl/Cl radical generated. HCl is a catalyst for the chain propagation reaction and the initiation step [11]. Scavenging cannot stop the degradation process completely since it is diffusion controlled. However, HCl scavenging considerably reduces the rate of degradation and avoids the very fast process that eventually causes PVC blackening. Stabilization is complicated by the fact that primary stabilizers are strong Lewis acid, reacting with HCl that catalyzes the initiation and propagation of PVC degradation. To avoid this, secondary stabilizers should be present to react with HCl to protect the primary stabilizers.

Assuming to use Ca Stearate here is reported the protection mechanism on PVC:

PVC-Cl + Ba-$C_{18}H_{36}O_2$ → PVC-$C_{18}H_{36}O_2$ + BaCl

The displacement of the allylic chlorine and creation of a stronger bond less prone to be broken affect the initial color of the article. In general the mechanism of protection for Ca/Zn systems is exactly the same of Ba/Zn and Ba/Cd.

Ca/Zn stabilisers deactivation of zip elimination mechanism

The deactivation of all species catalyzing the zip elimination consists of three reactions. The first consists of the neutralization of HCl by the secondary stabilizer (Calcium carboxylate) and relative formation of the weak Lewis Acid $CaCl_2$. The second reaction involves the first stabilizer (Zinc carboxylate) which consumes HCl and forms $ZnCl_2$, a strong lewis Acid. This deleterious reaction requires a third step in which the primary stabilizer is re-formed together with $CaCl_2$. In Fig 11 the final scheme of deactivation of HCl is reported:

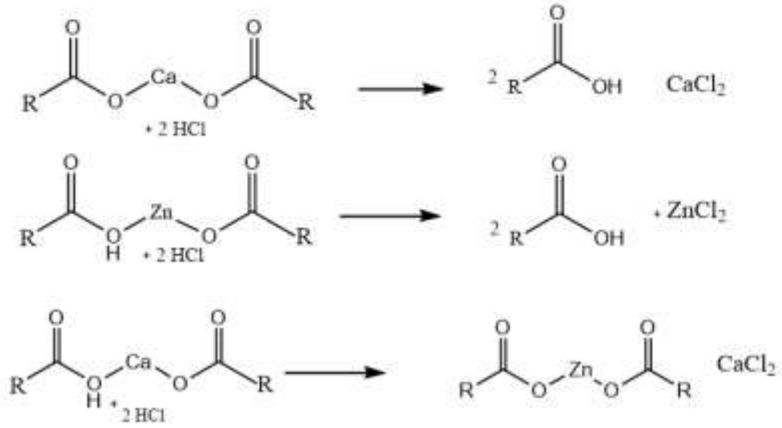
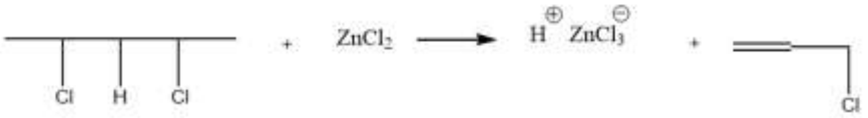


Fig 11: Ca/Zn carboxylate protection mechanism

Investigation of degradation mechanism of the Zn stabilizer

Thermal degradation of PVC has been studied using various techniques, among these UV-vis spectroscopy analysis is an important method by which you can determine the concentration of various polyene sequences. These are then related to the degradation process which is occurring in the film or in the solution phase. As previously reported Zinc carboxylate reacting with PVC leads to the formation of $ZnCl_2$ which is dangerous for PVC because acts like a catalyst for the dergadation process. Various workers [12.1] have showed that $ZnCl_2$ forms from $H^+Cl_3^-$ complex with the polyenic chain, as the amount of $ZnCl_2$ increases the “CED” (cohesive energy density) of the polymer reduces leading to the degradation of the material. Mechanism of degradation is reported:



Formation of degraded polyene sequences due to the degradation of Zinc stabilizer is called “Zinc Burning” and is catastrophic for the PVC discoloration that takes place after few minutes [12]. Calcium soaps delay the zinc burning but they are often not enough for getting a good “stabilization”[13], other players are needed.

Antioxidants

Antioxidants fall into two categories, depending on the mechanism of interrupting the degradation process. These are chain-terminating primary antioxidants or hydroperoxide-decomposing secondary antioxidants. More than one type of antioxidant can beused to produce the desired result bydifferent routes. Synergies between twoantioxidants can often produce betterresults than a single system at the sameconcentration.

Primary antioxidants react rapidly and are known as radical scavengers. The most important are sterically hindered phenolics and secondary aromatic amines. Hindered phenolics are high molecular weight antioxidants for polymers that are sensitive to thermal and oxidative degradation, due to formation of free radicals and peroxides.They protect against degradation at high processing temperatures and are highly efficient, low in volatility, and non-staining.They also have wide toxilogical clearance and are effective at very low dosages of typically 0.01-0.1%. Efficiency can be enhanced by using them with other antioxidants, such as phosphates and thioesters. They are normally available as free-flowing powders, but 50%aqueous dispersions are also available. There is a trend towards non-dusting products, including pelletized solids and liquids. They can be added to PVC plasticizers, where they can be dissolved, to inhibit oxidative degradation and embrittlement of PVC wire and cable insulation.

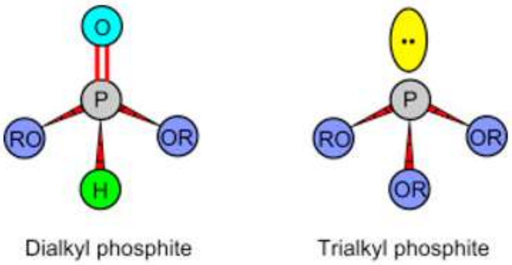
Secondary antioxidants react with hydroperoxides to produce non-radical products and are consequently often called hydroperoxide decomposers. They differ from primary phenols and amines in that they are decomposed by reaction with hydroperoxide, rather than containing it.They are particularly useful in synergistic combinations with primary antioxidants. Systems that do not contain a phenolic can provide good colour stability and gas-faderesistance, which are important properties in polypropylene fibres and other applications. Phosphite are oftenregarded as the most effective stabilizers during processing. They are able to protect both the polymer and the primary antioxidant.

Organic phosphites

Phosphorous acid, H_3PO_3, is the acid that forms when P_4O_6 reacts with water;

$P_4O_6 + 6\ H_2O \rightarrow 4\ H_3PO_3$

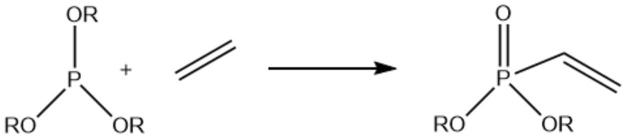
The hydrogen atom attached to phosphorous is not acidic so only two dissociation costants are present $Ka_1 = 5.1 \times 10^{-1}$ and $Ka_2 = 1.8 \times 10^{-7}$. Organic phosphites have the general formulas $(RO)_2PO(H)$ and $(RO)_3P$ and the structures of common alkylic phosphites are:



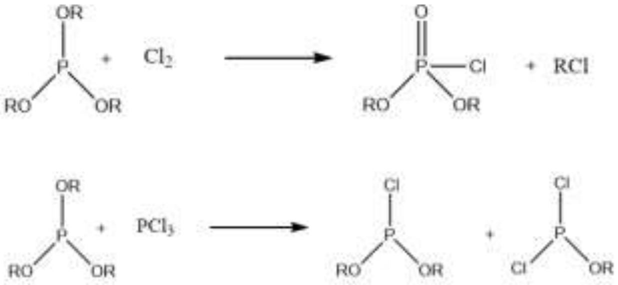
Because the trialkyl phosphates have an unshared pair of electrons on the phosphorous atom, they can function as Lewis bases and thus form complexes with metals. Phosphorous is a soft base so the complexes most often involve a soft metal atom or ion

Organic phosphites have roused special interest as stabilizing additives to PVC for preserving its original properties, they manage to preserve initial PVC color and transparency [14]. Organic phosphites are also effective in the effectiveness of primary antioxidants as thermal stabilisers. In combination with mixed metal stabilisers they manage to deactivate all species catalyzing zip elimination and to boost the long term thermal stability:

Then, they are capable to “repair” the formation of unsaturated species boosting the initial color and color hold:



It is well known that some high performance phosphite antioxidants are particularly sensitive to hydrolysis. It has two principle consequences: creation of potential handling issues as the product can become sticky and a possible loss in the performance of this type of antyoxidants [15] . Dialkyl phosphites for example once hydrolized give a monoalkyl phosphite or H_3PO_3, generally the rate of hydrolysis attack depends on the alkyl chain. Phosphites can be halogenated by reacting with Cl_2 or PCl_3



Sustainable PVC stabiliser development

ESPA represents the maiority of the PVC stabiliser producers across Europe. It includes the European Calcium Organic Stabilisers Association (ECOSA), the European Liquid Stabilisers Association (ELISA) and the European Tin Stabilisers Association (ETINSA).

As part of the VinylPlus, ESPA members have progressively replaced in the EU:

- cadmium stabilisers: completed in the EU-15 already by 2001 and by now in the EU 28

- lead stabilisers replacement: o RoHS compliance ; voluntary replacement in the other applications completed in EU-28 in 2015 o Replacement promoted worldwide and expanding

-Bisphenol-A (meanwhile included in the REACH Candidates List for Authorization): alternative formulations developed and available since many years.

Stabilisers formulations are being continuously adapted to anticipate on the regulatory context and with sustainability in the visor. VinylPlus is developing ASF, a voluntary, European-wide approach to assess the sustainability of PVC additives in various types of articles. ASF builds on available Life Cycle information (cradle to grave) and informed analysis by industry experts to provide a qualitative screening assessment of the relative performance of additives. The methodology is a complement to (and compatible with) schemes such as Environmental Product Declarations (EPD) and Product Environmental Footprint (PEF) but not positioned as a substitute for quantifiable product claims, it takes a wider perspective giving a clear picture of where to aim and what to do to improve additives sustainability performance. The sustainable product development is an iterative process (Fig 12) that aims to integrate sustainability principles in planning the future of chemicals reduces the risk of hitting regulatory barriers at a later stage, to give a clear interpretation of data coming from different stabilisers and to devote important resources to R&D to supply REACH ("Registration, Evaluation, Authorisation and Restriction of Chemicals") compliant and performing solutions to the PVC chain.

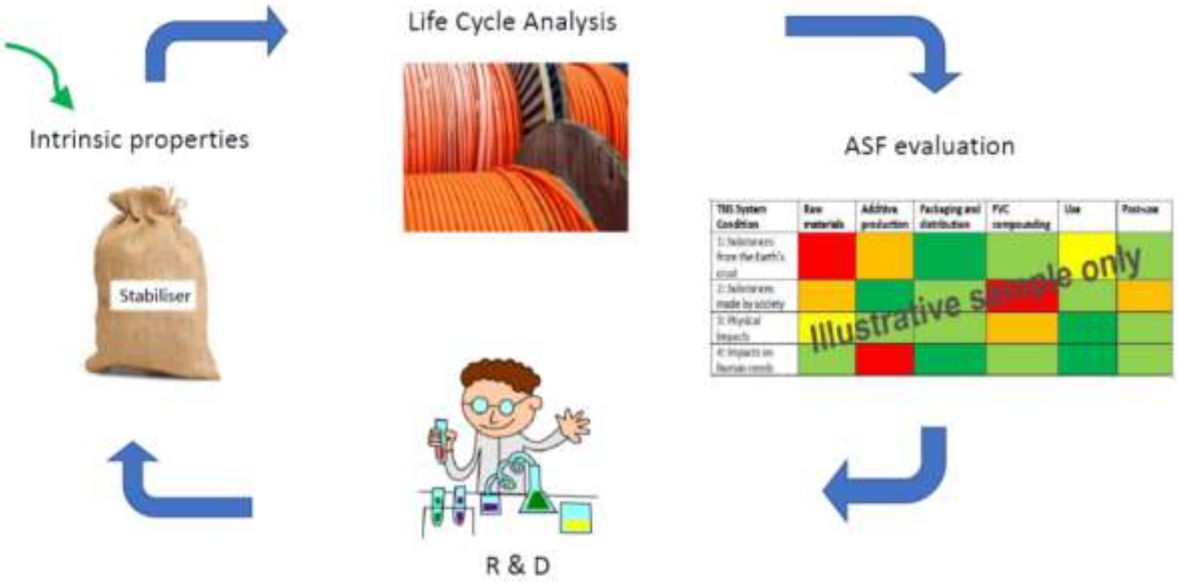


Fig 12: Sustainable approach scheme for PVC stabilisers

PVC Plasticizers (1.5)

Plasticizers are organic substances with various characteristics, whose main function is to intercalate the rigid polymer structures of material such as PVC for an easy movement and flexibility [16]. Generally plasticizers aim to decrease viscosity of polymers and the same for hardness, indeed they reduce the number of macromolecules contained in a unit volume and the Tg (Glass Transition Temperature) down to the room Temperature. Action of plasticizers is one of a lubricant, where the small molecules ease the movement of the polymer chains by pushing them further apart. They are used to produce soft PVC, usually mentioned with the acronyms P-PVC (plasticized PVC). Plasticizers influence physical-mechanical properties of PVC such as Elastic module, elongation at break, hardness and flexibility at low temperatures. They are used in a wide variety of PVC applications and so in electric cables, pipes, conveyor belts, car parts but also in many articles of clothing [17].

There are 3 important theories on thee mechanism of plasticization:

1) Lubricating theory → It is based on the fact that the physical domain is thin in one direction compared with the others. Plasticizer changes the polymer structure when rigth size molecules

go into the primary particles, weakening the interpolymeric forces through Van der Waals interactions, preventing the formation of the rigid networks after cooling.

2) Gel theory → It extends the previous theory suggesting that the plasticizers act by breaking the resin-resin attachment from each other preventing their reformation. The polymeric structure is maintained by the gel, an internal three dimensional honeycombstructure or gel.
3) Free volume theory → It gives to the plasticisation process a quantitative assessment, unplasticized PVC has a very little free volume, plasticizers increase free volume and allow to maintain it even at low temperatures. In P-PVC free volume can be increased by the motion of end chains or by changing functional end groups.

Primary plasticizers (phtalates) give the main plasticization and main characteristics to article while secondary plasticisers, (ESBO “Epoxidized soy bean”, Phospates and chloroparaffins) serve mainly to reduce costs, enhance thermal stability, impart a good behaviour at low temperatures, reducing smoke during combustion and reduce migration or extraction.

Phtalates plasticizers

They are characterized by a particular ease of manipulation and gelation and a high efficiency and volatility. They are the most used plasticizers type and in particular they are used for the production of electric cables for machines, electrical appliances, construction industry flooring and metal surfaces. Linear phtalates are outstanding in terms of low temperature behavior, weathering and volatility which decreases with the molecular size. High molecular weight (HMW) or high ortho-phthalates include those with 7-13 Carbon atoms in their chemical backbone, which gives them increased permanency and durability. The most common types of high ortho-phthalates are DINP (“Diisononyl phthalate” Fig 13) and DIDP (“Diisodecyl phthalate” Fig 14).

High ortho-phthalates represent just over 50% of the European plasticisers market. Risk assessments have shown positive results regarding the safe use of this group of substances. They all have been registered for REACH and do not require any classification for health and environmental effects, nor are they on the Candidate List for Authorisation. High phthalates are not mutagenic or toxic for reproduction, neither are they considered endocrine disruptors. Precautionary restrictions for toys and childcare articles which can be placed in the mouth exist for DINP and DIDP, based on liver effects at high doses observed in rat studies [17.1].

High ortho-phthalates are commonly used in PVC products such as wire and cables, flooring, truck tarpaulins, wall coverings, self-adhesive films or labels, synthetic leather, coated fabrics, technical foils, roofing membranes and automotive applications.

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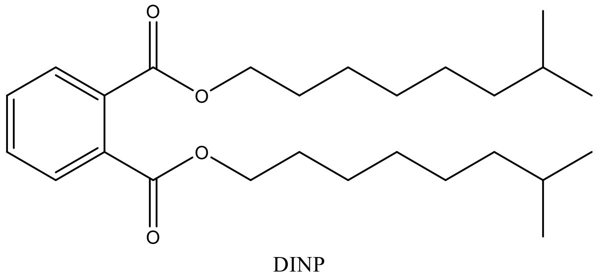


Fig 13 Diisononyl phthalate

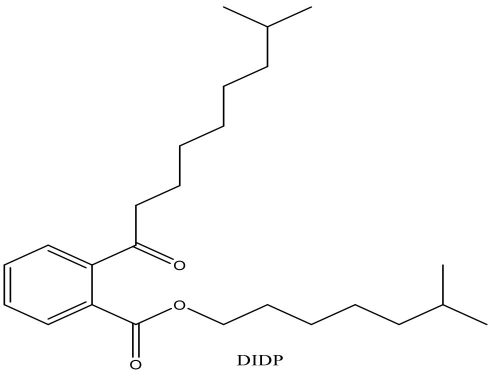


Fig 14 Diisodecyl phthalate

PVC flooring, a new dimension for PVC application (1.6)

PVC is commonly used for the production of flooring for homes because it provides inexpensive, easy to clean surfaces and is especially practical in kitchens, bathrooms and children's playrooms and bedrooms [19]. PVC flooring is constructed from soft PVC that has been plasticised to make it flexible. Phthalates are the most commonly used plasticisers for manufacturing soft PVC. Phthalates do not bind to PVC chemically, but are present as freely mobile and leachable components of the plastic matrix. Consequently phthalates are gradually lost from PVC over time by volatilisation to the air. Phthalates have a high affinity for particles and a recent study in Norway [21] showed that as well as vaporising to air, these chemicals were also present in suspended particles in air and in sedimented dust samples from homes. The study demonstrated that phthalates migrated from PVC flooring to sedimented house dust. For PVC floors, washing has also been shown to release phthalates into the water.

Historically, diethylhexyl phthalate (DEHP) has been the most commonly used phthalate but more recently there appears to be increased market use of di-isononyl phthalate (DINP) and di-isodecylphtalate (DIDP).

Biocide (1.7)

Biocidal products are active substances and preparations of microorganisms which serve to repel, render harmless, or destroy harmful organisms (pests like moths, woodworm, mice, pathogens, molds, etc.) and are not applied in agriculture [21.1]. The aim of biocide use is to prevent damage by harmful organisms to food, commodities, building materialss (wood), and other products and to guarantee hygiene in buildings. Biocidal agents are grouped in 23 different products types according to the different fields of application e.g, disinfectants, wood preservatives, rodenticides etc. A risk assesment has to be carried out for biocidal products and their active ingredients. This risk assesment covers environment, consumer health, and occupational safety and comprises the following steps:

-hazard identification

-dose (concentration)- response (effect assesment)

-exposure assesment

- risk characterization

Biocide regulations

Worldwide, environmental regulations are playing a significant role in the biocide market. In the European Union, the Biocidal Product Directive (BPD) requires registration of active ingredients by the end of 2008. Once registered, biocides will undergo a testing and review process. The BPD is viewed by the industry as being significantly more restrictive than U.S. EPA [Environmental Protection Agency] regulations.

“The positive impact of the BPD is that stronger products will come to the forefront. On the other hand, the costly process to register may stifle development of new biocides,” comments Tom Aroella, regulatory affairs manager at Thomson Research Associates [22]. In the U.S. biocides used as additives for material preservation must be registered with the EPA under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). Suppliers have become more aggressive in promoting use of biocides with end-users in applications that have human or food contact, therefore implying a health benefit, notes Mr. Babinsky. However, health claims are monitored closely by the EPA in the U.S. and increasingly by regulatory agencies globally, say industry experts. In the U.S., the Treated Articles Exemption of FIFRA allows a company to avoid the lengthy and expensive pesticide registration process, but they can not make explicit or implicit health benefit claims about the product and must state to customers that the biocide is solely for protection of the treated article. Suppliers take regulatory compliance very seriously, offering guidance to their customers on using appropriate claim language for the finished product. To support claims appropriately, efficacy of a biocide must be tested in the specific end-use application.

Biocides and Fungicides may be added to PVC flooring to prevent the growth of bacteria and fungi. These may include silver, ammonium bromide, mercaptobenzothiazole and isothizolinic molecules. Biocides impart an antimicrobial protection including external effects, and prolongation of product life. Biocidal chemicals used in flooring can be sensitizing and can also cause contact dermatitis and respiratory irritation [17]. In the case of non-carpet flooring, physical removal is often as effective at bacterial removal as the inclusion of a biocide. Before you purchase flooring with a biocide, you should consider whether you really need it or not.

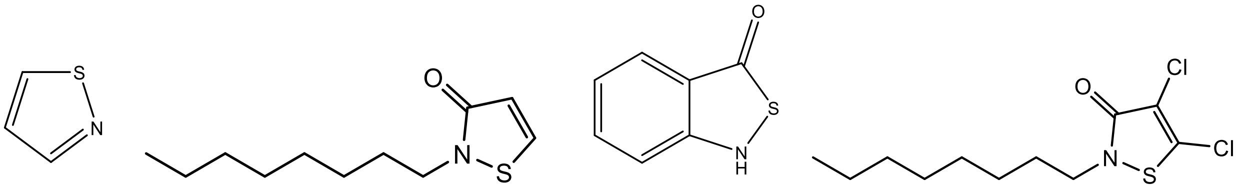
The majority of pure polymeric materials are relatively resistant to biological attack. However, under suitable conditions, microbial growth, such as fungi, algae and bacteria, can be observed on polymeric materials. While fungi type microorganisms seem to be predominant in colonizing the surface of such materials, algae growth has also been observed in some situations. Frequently, the source of food supporting this growth is non-polymeric additives o r components, polymer monomers, other material additives, by-products of environmental degradation, foreign contaminants trapped on the plastic surface, etc. Only certain polymers, such as for example cellulose or cellulose derivatives, aliphatic polyesters (for example polycaprolactone and polylactide), and certain polyurethanes, seem to be susceptible to direct microbial attack and degradation of the main polymer chain. Other materials could be introduced within this continuous phase such as, for example, particles of other polymers or organic matter including natural products, minerals or metals, gases or liquids. Plastics, rubbers, coatings, sealants and adhesives are all examples of polymeric materials. Fungal growth on polymeric materials can cause a loss of material properties such as flexural strength, tensile strength or elongation at break, loss of surface integrity, significant discoloration, odor or unpleasant appearance. The development of a new generation of environmentally friendly materials, such as for example plastic filled with wood, with increased susceptibility to fungal attack creates a strong need for better protection of such materials. Photodegradation of the biocide is a very important problem for perservatives activity and for the environment, furthermore is known that biocides leach from facades with rainwater and end up in the environment via stormwater runoff. These polymeric materials that are sensitive to fungal attack require a more efficient, environmentally friendly and cost effective biocidal system. Furthermore, fungi, algae and / or bacteria growth on such materials presents aesthetic problems and can create slick, unsafe surfaces where these materials are used in walking surfaces. To protect polymeric materials against fungal attack, the addition of biologically active compounds (fungicides) is required. In the case of thermoplastic resin, the fungicide must be compatible with all ingredients of the resin system and thermally stable at typical processing temperatures. Furthermore, it should be cost effective, non-toxic, easy to handle and store, safe for the environment, and it should not give an undesirable color or odor to the thermoplastic resin product. Organic fungicides are usually very expensive and can be toxic to the environment and sometimes to some degree to humans. Addition levels up to 10% in the polymer matrix may be required to control fungal growth in some situations, depending on the product, product service conditions, and required protection level. In situations where a significant amount of fungi degradable component is present, the typical quantity of biocide may not always be sufficient. Such processing requirements make the selection of fungicides a difficult task, as the temperature stability of the fungicide must also be considered. Furthermore, many polymeric materials are intended for service in exterior conditions where direct expo sure to water or ultraviolet light must be expected. This makes selection of fungicides even more difficult. Generally, in such exterior conditions, fungicides with a higher level of resistance to degradation by ultraviolet (UV) light are required which significantly increases the cost of protection of the polymeric materials against fungal attack [25]. Formulations designed and optimized for use in protected environments are frequently not fully effective for exterior use. [26]

The importance of isothiazole and of compounds containing the isothiazole nucleus has been growing over the last few years. Isothiazolinones are used in cosmetic and as chemical additives for occupational and industrial usage due to their bacteriostatic and fungiostatic activity. Despite their effectiveness as biocides, isothiazolinones are strong sensitizers, producing skin irritations and allergies and may pose ecotoxicological hazards. Therefore, their use is restricted by EU legislation.

Organic compounds containing five-membered heterocyclic rings play an important role in many industrial sectors. Among them, isothiazole and its derivatives have found applications in different fields since they present useful biological properties, such as antimicrobial, antibacterial, antifungal, antiviral, anticancer, and anti-inflammatory activities. Furthermore, isothiazoles have been described to act as inhibitors of proteases for the treatment of anxiety and depression, as inhibitors of aldose reductase, and as 5-hydroxytryptamine receptor antagonists.

Chemically, isothiazole (1,2-thiazole) is a five-membered heteroaromatic that is considered to be derived from thiophene, in which the second position is occupied by a nitrogen atom Isothiazol-3-

ones are known for their remarkable antifungal and antibacterial properties, being extensively used as biocides in a variety of industrial water treatment applications for the control of microbial growth and biofouling. They have also been recommended as preservatives to prevent fungal growth in a wide range of manufactured goods, such as emulsion paints, wood varnishes, adhesives, and natural and artificial leather. The isothiazolinones most commonly found in commercial applications, alone or in combination, are methylisothiazolinone (MI), methylchloroisothiazolinone (MCI), benzisothiazolinone (BIT), octylisothiazolione (OIT), and dichlorocthylisothiazolinone (DCOIT). [Fig.15].



isothiazole 2-Octyl-2H-Isothiazol-3-One benzisothiazolinone 4,5-dichloro-2-octyl-2H-isothiazol-3-one

Fig *15: Most widespread isothiazolinones present in market*

DCOIT, the best biocide for PVC applications (1.8)

DCOIT [A] (Fig. 16) is a fungicide bactericide for interior/exterior plastics.

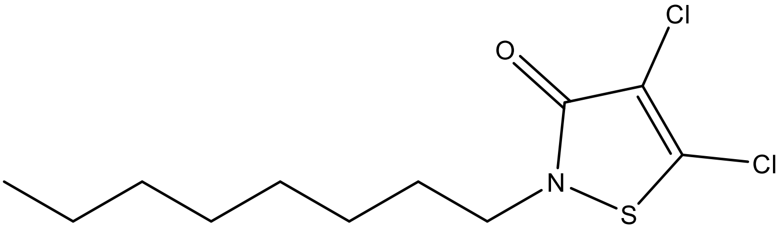


Fig.16 "DCOIT"

Its active ingredient control bacteria that cause architectural paints and coatings to degrade and prevents mildew growth after the films dry. At the same time, DCOIT industrial microbicide has low water solubility, making it very resistant to being leached from the paint film by ambient moisture. Furthermore, DCOIT does not have the same environmental and toxicity issues associated with other biocides for example it is considered much more green than mercury – based biocides. DCOIT controls a wide range of microorganisms, including fungi, algae and bacteria. As far as fungi are concerned, this isothiazolinone product inhibits the growth of many species at low use levels. Its efficacy against Aureobasidium pullulans (the fungus predominantly responsible for the development of mildew in exterior paints) is particularly noteworthy. Equally important from the stand point of in-can protection, this biocide also is very effective against the bacteria, especially the Pseudomonas species, that attack paints, joint compounds, roof coatings, exterior insulating and finishing systems (EIFS), and clear finishes in the can.

In addition to its impressive antimicrobial capabilities, DCOIT has a number of other appealing features for formulators. Because of its isothiazolinone chemistry, it is non-persistent in the environment, breaking down readily into harmless compounds. In addition, this biocide does not release formaldehyde, does not require zinc oxide for mildewcide stability and is easily incorporated into paint and coatings formulations. The new biocide can be used in both latex- and solventborne paints. With all its performance benefits, DCOIT exacts no appearance or performance penalty. This compound will not cause a paint film to yellow, will not destabilize a paint or detract from its tint retention and is EPA-registered for use in coatings.

Impurities occur naturally from minor by-products of the production process such as amines (DCOIT is made with Octylamine). Most common end uses of DCOIT are exterior usage, as it is also effective against algae and insects in addition to conferring both anti fungal and limited antibacterial effects. It’s characterized by good UV stability and so it’s ideal for permanently or often saturated products. Furthermore once released to the environment is really degraded.

Vynyl floors

Vynil floors, also known as “linoleum” are present in many contexts like hospitals, schools or in the gym. They are very developped in the market because they are very easy to clean and their lifespan is high compared to other types floors.

Generally three kinds of vinyl floors are available in the market. The first is the floating floor, which involves the dry laying of the tiles on a mat that acts as an interface on the floor below. This differs from raised floors which involves the laying of actual tiles physically detached from the undrlying support as they rest on a special feet. Peculiarity of vinyl floors is that you can recreate lots of geometries and various effects and the practice usually involves an interlocking laying method, thickness is minimal (3-4 mm) and it can be cut and worked with a simple cutter by arming ourselves with a square for regular square cuts. The third possibility of vinyl floors is adhesive, in which can be put directly to the undrlying substrate and are also suitable for wall cladding.

AIM OF THE THESIS (2)

An important customer of Reagens (one of the most important producer of PVC stabilisers) which sell vinyl floor had a problem with PVC floor and asked to Research and Development department to resolve it. The PVC floor is made of overlapping layers that confere the transparent appearance to the whole structure. The vinyl floor in warehouse and during the transporting procedures is kept in a spiralized structure in which the layers come in contact each other. Gerflor noticed that in the formulation containing the Ca/Zn stabiliser and DCOIT biocide [A] (the fungicide described in the introduction) some layers turned yellow, thus changing the color of the entire vinyl floor.

Aim of the experimental thesis is multiple, first of all to understand which of the stabilisers components reacts with DCOIT provoking the yellowing issue, then to identify the product of reaction and at the end change the formulation of the stabiliser in such a way to mantain the transparency even in presence of the DCOIT biocide. Considering that was not possible to clearly identify which of the different layers turned yellow due to the possibility of a color diffusion through the structure, the analysis were performed on the top coating, the visible layer, that has to be the most transparent layer because it’s in surface of the vinyl floor.

RESULTS AND DISCUSSIONS

BIOCIDE AND STARTING Ca/Zn STABILISER (3.1)

In laboratory 3 types of DCOIT are present:

-DCOIT dissolved in diisononyl phtalate plastificant (“PDN”) composition 20% m/m

-DCOIT dissolved in diisodecyl phtalate plastificant (“PDP”) composition 20% m/m

- DCOIT pure at 98%, solid

The three biocides were used during the experimental part for the formulation of an alternative PVC stabiliser formulation.

Considering the hypotetical reaction that leads to the yellow color:

$$A + B \rightarrow C + (D?)$$

Where A is the DCOIT, B is a component of the stabiliser, C is the product of reaction and D is another possible coproduct in order to evaluate which part of the stabiliser reacts with the isothiazolinic ring was decided to divide the stabiliser in all components separately and to evaluate the interactions with the biocide.

The Ca/Zn PVC stabiliser (STAB “A”) consists of:

STAB A	grams
oxoel	8,22
Versatic Acid	5,22
Benzoic Acid	2,44
Calcium hydrate	0,35
Zinc Oxide	1,65
chel 704	70
Refined soybean	10,29
A76	2,2

-A 76: Antioxidant

-chel 704 : Triisotridecylphosphite, in alternative chel 210 (Diisodecildiphenylphosphite can be used)

PRELIMINARY PROBES (3.2)

Spectrophotometric analysis were runned in order to perform colorimetric test. Uv-vis spectrophotometer was used to determine the shade of the yellow color, Gardner color of the various species was measured.

Gardner color system is a particular scale used to measure the yellowness of a sample in order to find out the quality or the aesthetic appeal of different substances. The sample is placed in a plastic cuvette and the measurment is quickly carried out using illuminant C (standard use to compare colors and images), then the % transmittance is automatically measured and this result is converted to a number in the range 1-18 that corresponds to a value on the Gardner color scale.

Fig 17 Gardner color scale comparator

In Table 2 are reported the Gardener color values of the single components while in table 3 first PDN then PDP are added to the single components and the color darkenin was evaluated at a constant intervals of time in such a way to understand which of the species improve more the starting coloration. Components were added to PDN and PDP always in 1.1 ratio (mass).

species	color
pdn	2.1
pdp	0.5
CHEL 704	0.8
CHEL 210	0.9
Zn v basic	0.0
Ba/Zn soap	6.0
Ca/Zn soap	0.1

Tab 2: Gardner color of species alone

#PDNmix	0'	30'	60'	120'	24h	48h
CHEL 704	6.4	6.7	7.1	7.7	8.8	
CHEL 210	6.9	7.2	7.4	7.5	8.4	
Zn v basic	0	0	0	0	0	0
Ba/Zn soap	1.5	4.6	4.8	5.5	6	
Ca/Zn soap	2.0	2.5	2.7	3	3.5	

#PDPmix	0'	30'	60'	120'	24h	48h
CHEL 704	5.8	5.9	6.2	7.2	8.3	9.2
CHEL 210	4.3	8.4	8.6	8.8	9.8	10.6
Zn v basic	0	0	0	0	0	0
Ba/Zn soap	3.5	5.3	6.0	6.0	6.5	
Ca/Zn soap	1.0	1.5	1.7	1.7	1.7	

Tab 3: Gardner color of the species mixed with PDP and PDN and evaluation of the darkening after constant intervals of time

From spectrophotometric tests seems that phosphite species are those that enhance more the coloration of the blends with DCOIT, for this reason the hypothesis of a chemical reaction between the phosphite and the isothiazolinic ring is to take into account. Other components seem not to influence considerably the color of the mixtures.

IR TESTS (3.3)

In order to corroborate the hypothesis of phosphite involved in a chemical reaction IR analysis were carried out. The idea was to overlap absorbance spectra of phosphite, DCOIT and product of reaction in order to confirm the theoretical formation of the yellow compound. Considering the inertia of plasticisers was decided to use “pure” DCOIT (98% m/m), a white powder analyzed with FTIR/ATR (“attenuated total reflectance”) technique.

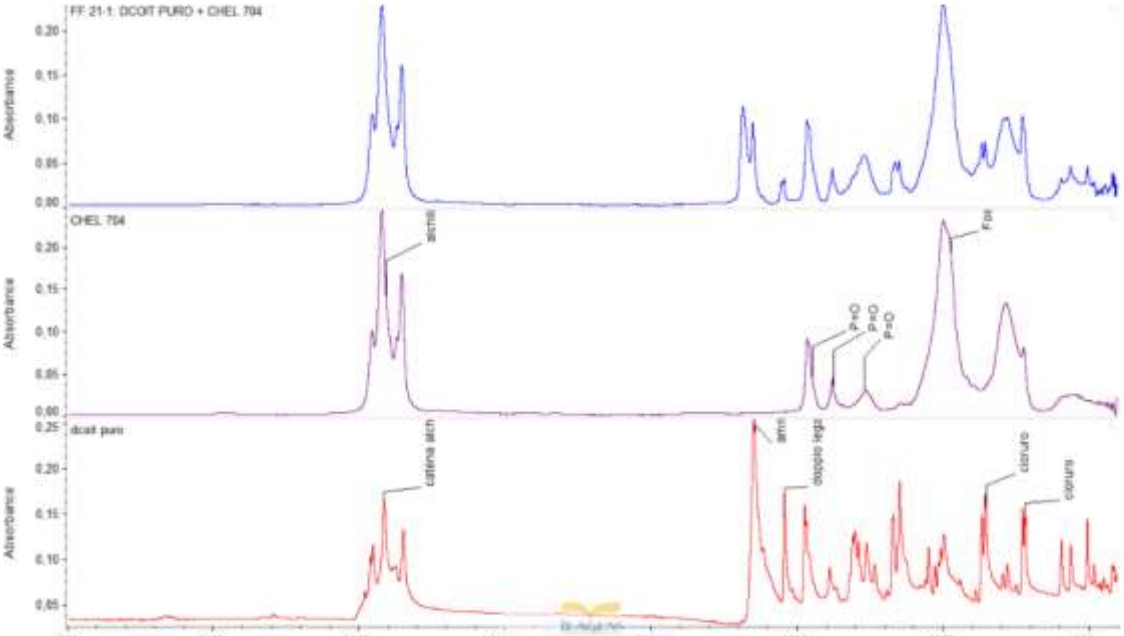


Fig 18: Absorbance spectrum of DCOIT, CHEL 704 and both mixed

Analyzing the first IR (Phosphite + DCOIT) is possible to see the formation of a 1700nm peek that is absent in the phosphite and in DCOIT, this withnesses the reaction between the phosphite and the isothiazolinc ring. Furthermore the peek of the amide (1680 nm) of isothiazolinic ring disappeared so it’s possible to hypothesize a mechanism of a nucleophilic attack that breaks the ring and so the structure of DCOIT. As reported in the introduction isothiazolinic organic chemistry is quite complex [27] so it’s not immediate to identify the product of reaction with CHEL 704. Considering that phosphites contain free alcohols that come from their synthesis, the possibility of a nucleophilic attack performed by the aloholic part of the phosphite was real. For this reason the alcoholic fraction of

CHEL 704 (a mixture of C12 and C13 industrially named “ISALCHEM 123”) was isolated and added to DCOIT in (1 : 1 mol) (Fig 19)

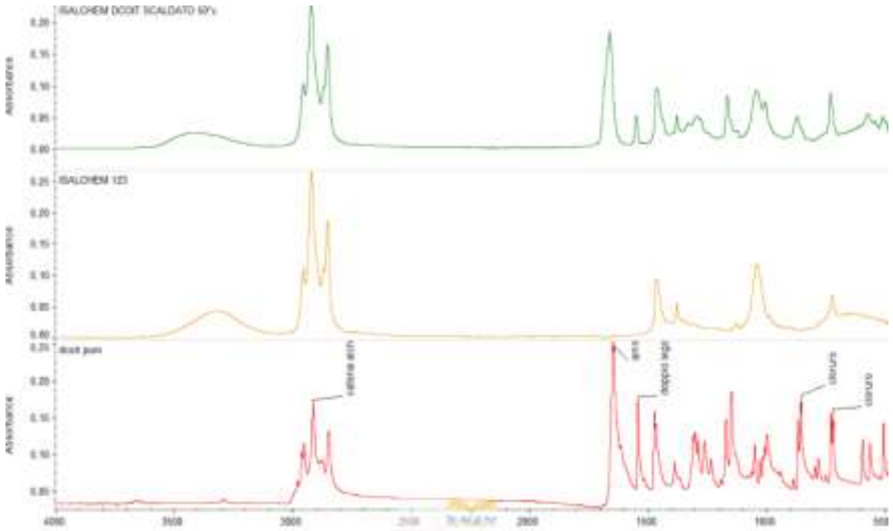


Fig 19 Absorbance spectrum of DCOIT, ISALCHEM 123 and both mixed stacked spectra

Comparing the three spectra, the 1700 nm peak is present thus withnessing a possible attack of the alcohol.

The same procedure was applied for the other phosphite, CHEL 210, and its relative free alcoholic part, Phenol. Notice that again the peak that confirms the chemical reaction is present at 1700 nm. (Fig 20, Fig 21)

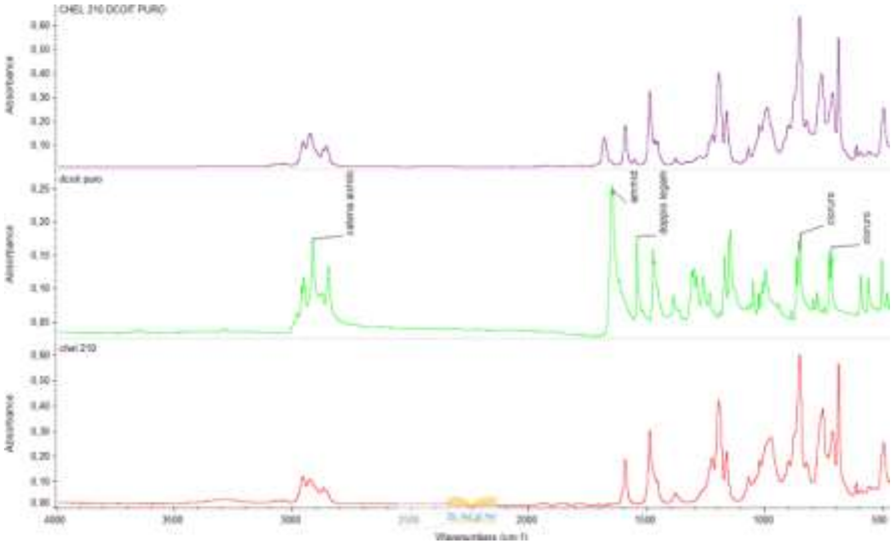


Fig 20: CHEL 210 + DCOIT stacked spectra

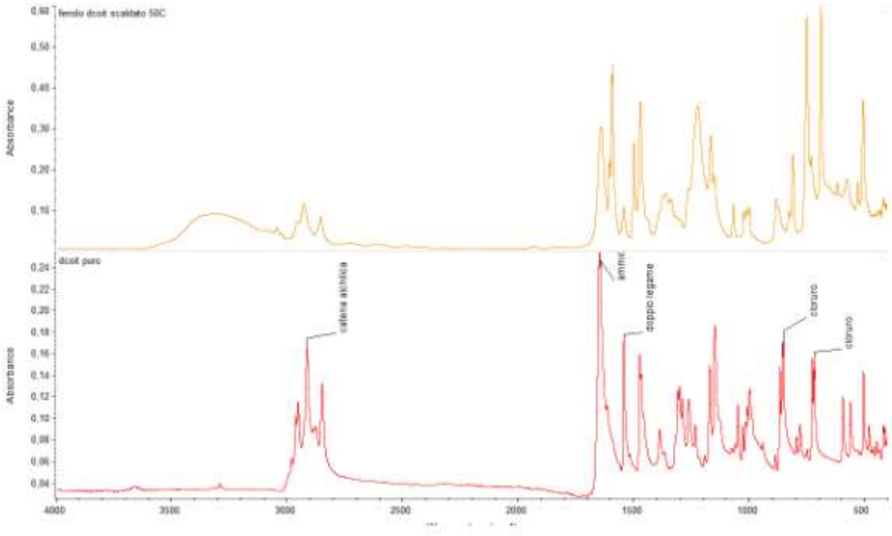


Fig 21: absorbance spectra of phenol and phenol+DCOIT stacked

After having confirmed that phosphite and its free alcoholic matrix (A) reacts with the biocide (B) the following step is the identification of the product of reaction. This is a complex task because the kinetic of reaction is not clear, to simplify the matter the formation of two products has been supposed, the first (C) comes from the phosphite that reasonably underwent chemical modifications and the second (D) represents what remains from the DCOIT that has been attacked.

$$A + B \rightarrow C + D$$

Concerning the mechanism is possible to hypothesize a nucleophilic attack of the phosphite/alcoholic part to the sulphur atom, nucleophilic cleavage of the S-N bond is reversible as reported in literature [27](Fig 22)

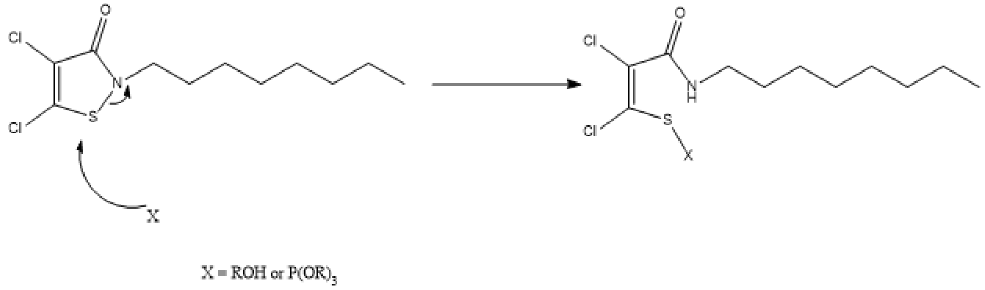


Fig 22: breakage of the isothiazolinic ring due to nucleophilic attack

An organic synthesys of DCOIT and ISALCHEM 123 has been carried out [*], the purpose was to investigate accurately the mechanism of reaction and mostly the identification of the product, previously the biocide and alcoholic chain were mixed using in 1:1 ratio now ISALCHEM was added in excess.

An ATR-IR analysis (Fig 23) was performed in order to check the presence of the reaction product and this was confirmed, is possible to notice that the reaction took place even if “yellowing” didn’t occur.

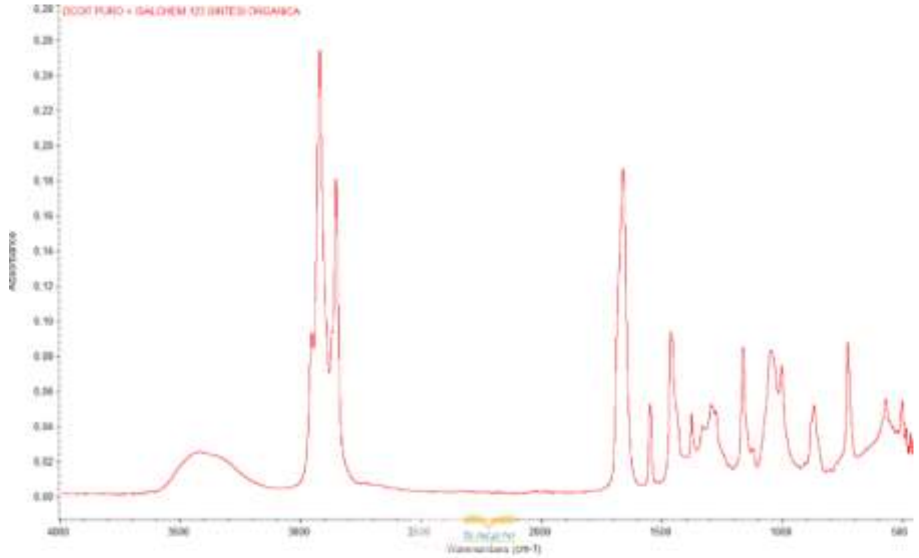


Fig 23 FTIR-ATR of ISALCHEM 123 + DCOIT in controlled conditions

GC-MS TESTS (3.4)

In order to investigate the nature of the reaction product a GC-MS analysis was carried out. The crystal was filtered with buchner and kept 2 h in a stove in order to evaporate the solvent.

Firstly DCOIT and ISALCHEM 123 were dissolved in N-isodecane in order to understand the possibility of the biocide to be eluted, GC results are here reported (Fig 24):

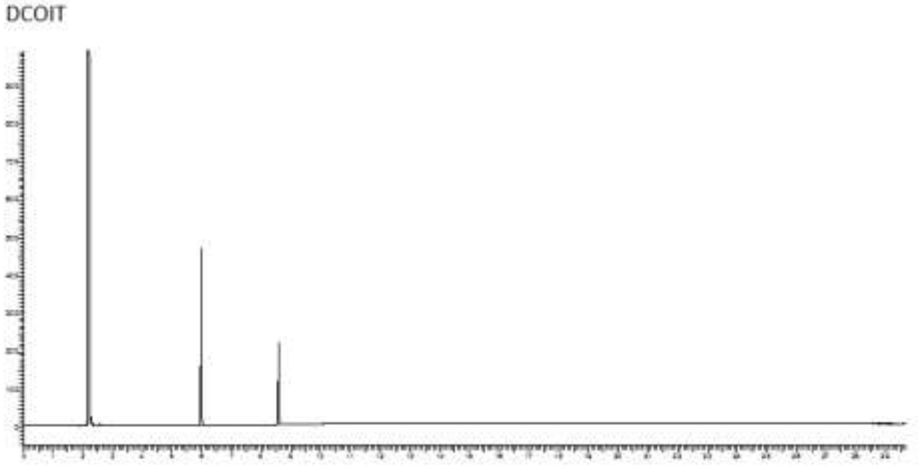


Fig 24: GC of DCOIT

In the spectrum is possible to see the peak of Toluene (solvent) at 2.1 seconds the N-isodecane at 6.0 seconds and DCOIT at 8.5 seconds.

Before running the GC the product was filtered with buchner to remove impurities.

Then GC-MS analysis of the white solid was performed, overlapping the GC-MASS spectra of the reaction product (Fig 25) is possible to see the not reacted DCOIT (8.5 seconds), the ISALCHEM (comprised between 4.5 and 6 seconds) but not the product of reaction, this means that the product of reaction is not detectable with GC-MS the alcoholic mixture and the biocide have actually reacted, the previous ATR spectra testifies it, but the product can not be eluted at GC.

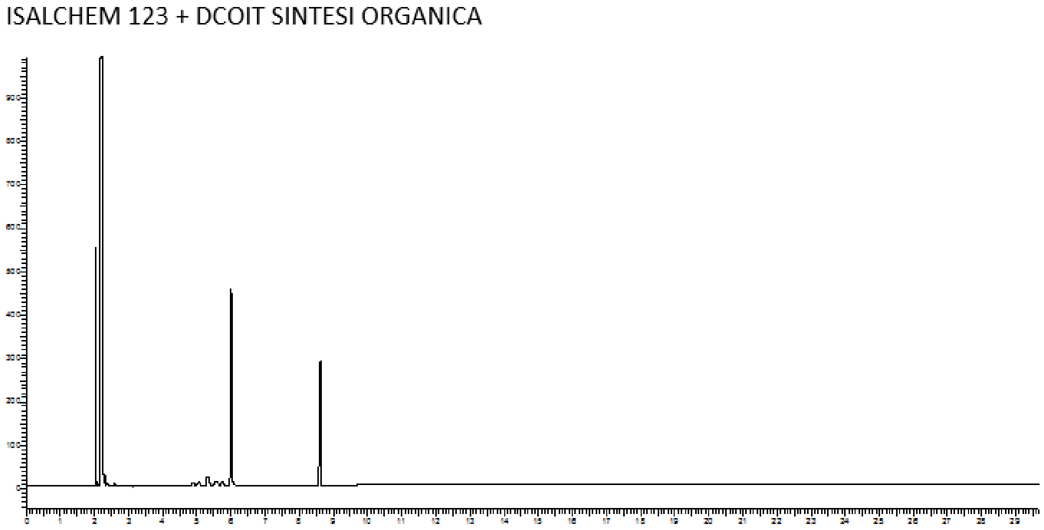


Fig 25 GC of ISALCHEM 123 + DCOIT

An organic synthesys of DCOIT and chel 704 has been carried out at the same conditions as the previous reaction, with chel 704. DCOIT and chel 704 were added in a large volume of CH2CL2 solvent in order to minimize their contact and prevent from the yellowing. After 10 minutes stirring the solution turned yellow and after one hour the solution was completely red. (Fig 26) After one night at environmental Temperature with no agitation the products presents as a black homogeneous liquid. (Fig 24). Is useful to remember that CHEL 704 is dissolved in ISALCHEM 123 and for this reason at least two reactions should have taken place, the first with the alcoholic chains and the second with the phosphite.

Fig 26 CHEL 704 + DCOIT after 10 minutes (left) and after 24 hours (right)

After having confirmed the presence of the usual peak at IR (Fig 27) a GC-MS analysys of the mixture was carried out (Fig 26) , also in this case no peaks related to the product of reaction were detectable because the peak at 2.0 seconds is the CH_2Cl_2 and that at 8.5 seconds represents the DCOIT that has not reacted with the phosphite.

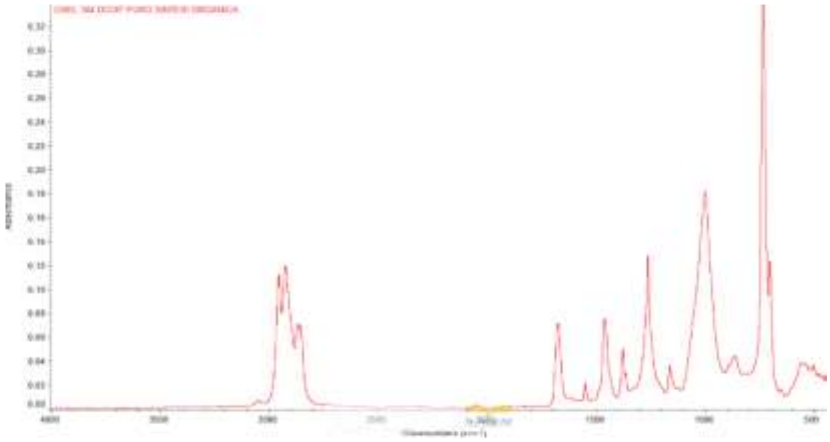


Fig 27 DCOIT + CHEL 704

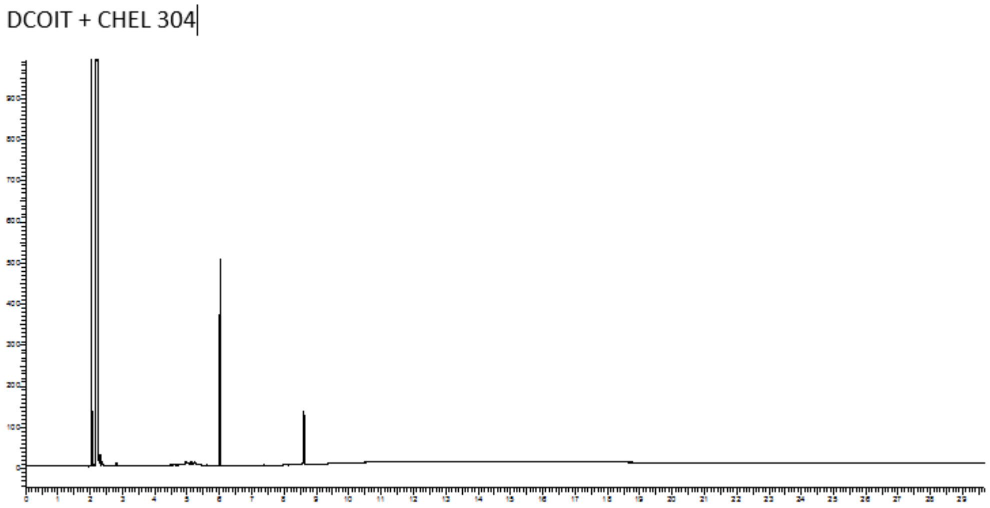


Fig 28 GC MS DCOIT+ CHEL 704

In order to investigate the nature of the products coming from the reaction of DCOIT with CHEL 704 (R) and ISALCHEM 123 (I) a TLC has been performed, as eluent agent a mixture 1:1 of $CHCl_3$ and Hexane was used. “I”, “R” and DCOIT diluted with CH2CL2 “D” have been run on the plate and analyzing with UV lamp was possible to confirm that DCOIT completely reacted in both cases.

LIQUID CROMATOGRAPHY TO IDENTIFY OF THE BLACK PRODUCT (3.5)

Focussing on the reaction of DCOIT and the phosphite a liquid chromatography has been performed, idea was to separate all the components present in the black product in order to analyze them separately. As stationary phase Silica gel was used and in order to elute the column 1 L of CHCL3 and CH_2Cl_2 was prepared. In Fig 29 the column at the beginning of the separation is shown

Fig 29: LC

7 fractions were collected, at a distance of 30’, and analyzed with TLC after having been put on the rotavapor, they were put on the same plate of “D”, “I” and “R”, under UV irradiation all the fractions (Fig 30) were present except the first three fractions, this probably was due to the excessive quantity of solvent was present for this reason they were combined together in the same reaction flask and after the treatment with rotating evaporator a stain at the same height of “R” was present, thus withnessing that the product of reaction elutes in the first 90 minutes of chromatography.

Fig 30: TLC

The organic synthesis of CHEL 704 and DCOIT was repeated at environmental Temperature in order to evaluate if it was possible to minimize the “yellowing effect” decreasing the kinetic of reaction. Again CH2Cl2 was used as solvent because it’s very volatile and so is very easy to remove it at the end of reaction. Again the phosphite was put in 20% excess respect the biocide and 40.96 ml of solvent were used. Even if the T was kept low the reaction betwween the fungicide and the phosphite started but th coloration happears much more faint. Analyzing with IR the product of reaction the spectra (Fig 31) is naturally the same but the peak at 1700 nm results less intense.

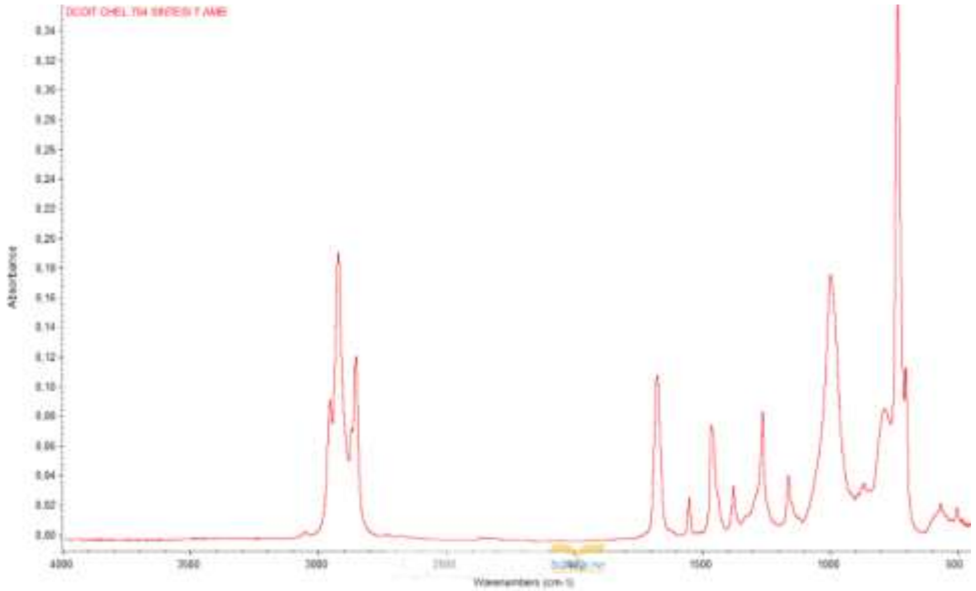


Fig 31: IR of DCOIT + CHEL 704 (20°C)

It was decided to perform a TLC to the product formed after 30 minutes and after 1 hour and as reference “D” and “I” have been run in the plate. This time as eluting agent 100 ml of CHCl3 were used, the stain of DCOIT didn’t happear and so is possible to hypothesize that it was fully converted to the final product. The fact that the color of the reaction mixture became always more intense leads to the hypothesis that consecutive reactions between the DCOIT and the phosphite take place.

USE OF AN ALTERNATIVE PHOSPHITE (3.6)

Assuming that the reaction involves S-N bond (see Fig.19), the idea was to find something that avoids the breakage of this bond in order to preserve both the biocide and the stabilizing agent. Considering the complexity of the situation was decided to use another kind of phosphite in solid phase “Distearyl Pentaerythritol Diphosphite” (Fig. 33), commercial name WESTON 619, known for its properties of UV stabilizing properties.

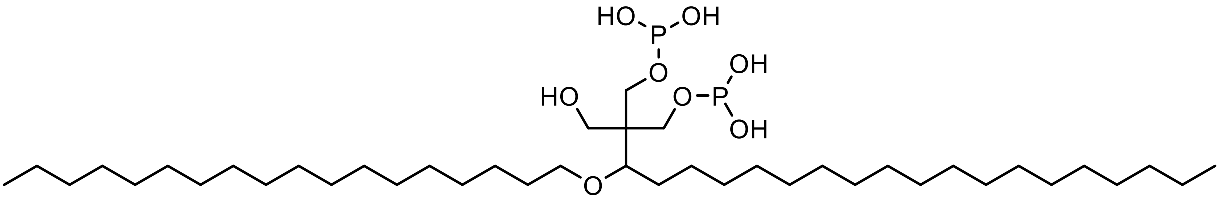


Fig 32“Weston 619”

Performing the reaction between this new phosphite and DCOIT was clear that the WESTON was much less reactive than CHEL, in fact a tenuous yellowing took place was evident that WESTON

619 reacts less than CHEL with the biocide but anyway leads to a not acceptable coloration , furthermore it costs much more than the other phosphite.

Fig. 33 reaction product of WESTON 619 + DCOIT after 2

OPTIMIZATION OF THE STABILISER FORMULATION (3.7)

Considering that every Phosphite used (CHEL 704, CHEL 210, WESTON 619) interacts significantly with DCOIT either breaking the isothiazolynic ring either breaking itself was decided to modify the composition of the Ca/Zn stabiliser. The purpose was to find an alternative formulation for the STAB "A" (Ca/Zn stabiliser) that didn't undergo yellowing issues by changing the Ca/Zn composition or if necessary to eliminate the phosphite. Following formulations were prepared:

1) Double soap Ca/Zn stabiliser with 60% CHEL 704 (STAB A 2)
2) Ca/Zn stabiliser with higher level of Ca and 60% CHEL 704 (STAB A 3)
3) Ca/Zn stabiliser with higher level of Zn and 60% CHEL 704 (STAB A 4)
4) Ca/Zn stabiliser without CHEL 704 (STAB A 5) with an high Ca/Zn (7.6% Ca 1.7%Zn) ratio, the aim was to make a formulation similar to Ba/Zn stabilisers that are more powerful than Ca/Zn and are characterized by a low degree of Zn.

STATIC THERMOSTABILITY TEST (Ca/Zn) (3.8)

Thermostability tests are performed in order to simulate thermal stress that affects the material during the production phase of the manufacture. Ca/Zn stabilisers (gel width 7 mm) are fixed on the sliding trolley of a WERNER MATHIS (Fig 34) thermostat oven at 200°C equipped with a constant speed trolley ejection system. Ejection rate was set to 0.5 cm every 60 seconds, which means that the 27 cm long samples took 54 minutes to completely exit the oven.

Fig 34:Thermostat oven MATHIS

Results of the tests are gradually degraded samples that show a progressive deterioration due to the protract heat exposure. The sooner the initial color get yellow the worser will be the stabiliser

Here are reported the results of "A" stabilisers first without biocides, then in presence of DCOIT dissolved in DINP (stab:DCOIT=3:1)(Fig) then in presence of Ottilisotiazolinone "OIT" (stab : DCOIT = 3:1) dissolved in DINP (Fig). Results (Fig 35, 36, 37) show that the formulation without Phosphite undergo a soft yellowing compared with the others, not depending on the presence/absece or kind of Biocide.

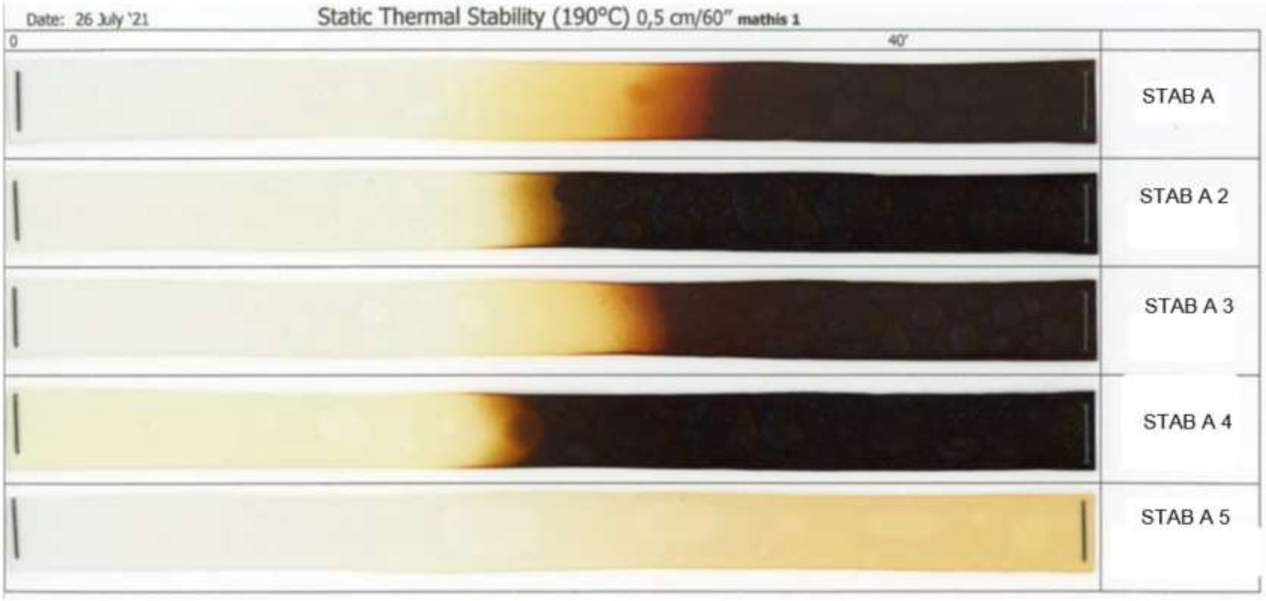


Fig 35: Static Thermostability test of formulation without biocide

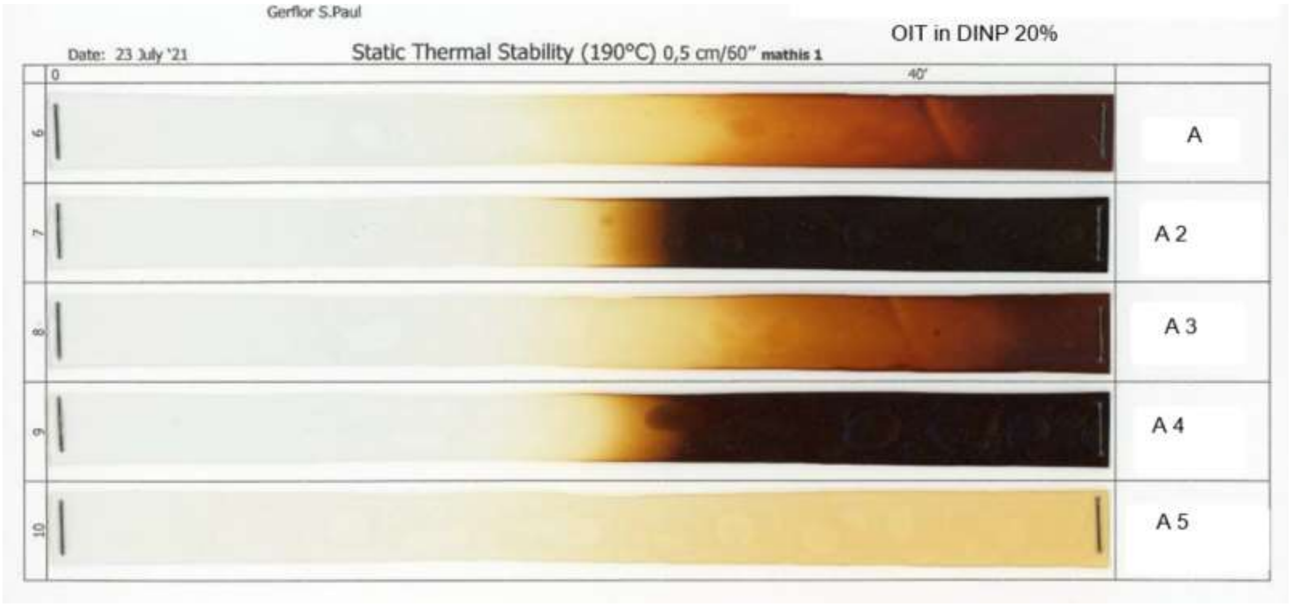


Fig 36: Static Thermostability test of formulation with 20% OIT

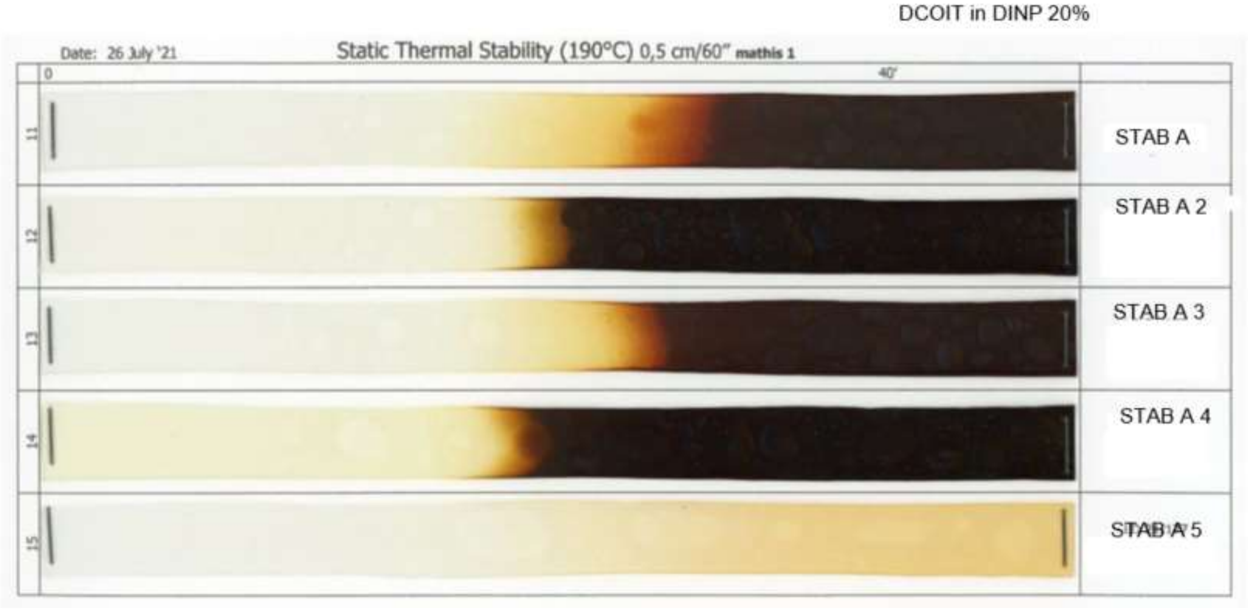


Fig 37: Static Thermostability test of formulation with 20% DCOIT

OVEN AGEING TESTS (3.9)

Was decided to perform ageing tests in order to speed up the degradation of the material and evaluate the effective power of the stabilizing formulations. The same formulations of the static thermostability tests were heated at 50°C for 4 weeks, then the CIELAB color space was measured. CIELAB, or Lab model (Fig 38), is one of the most diffused color space for the object color misuration. In this model "L" indicates the brightness, "a" stands for red and green and "b" stands for blue and yellow. (Fig) . In general the center of the sphere is achromatic and the saturation of the color increases along the axis. For the purposes of this scientific study we are interested in the variation of the yellow color and so the "b" coordinate, thee other parameter of interest is "De" value which indicates the mean quartic difference along the 3 axis. (De($_{ab}$)=[(L*)2 + (a*)2 + (b*)2] 1/2)

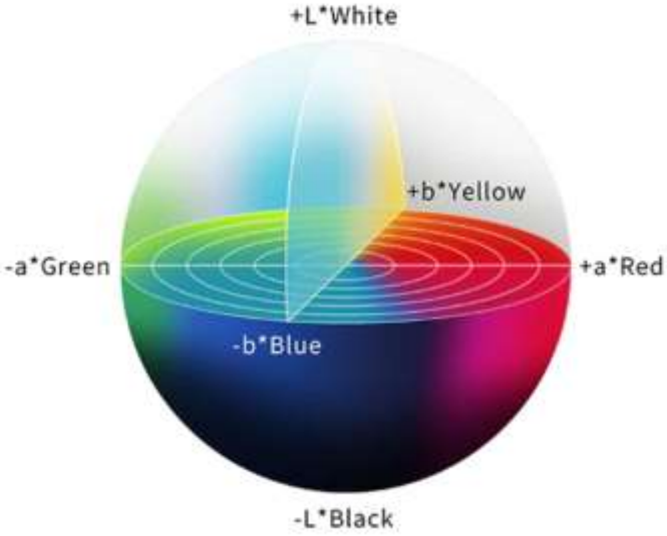
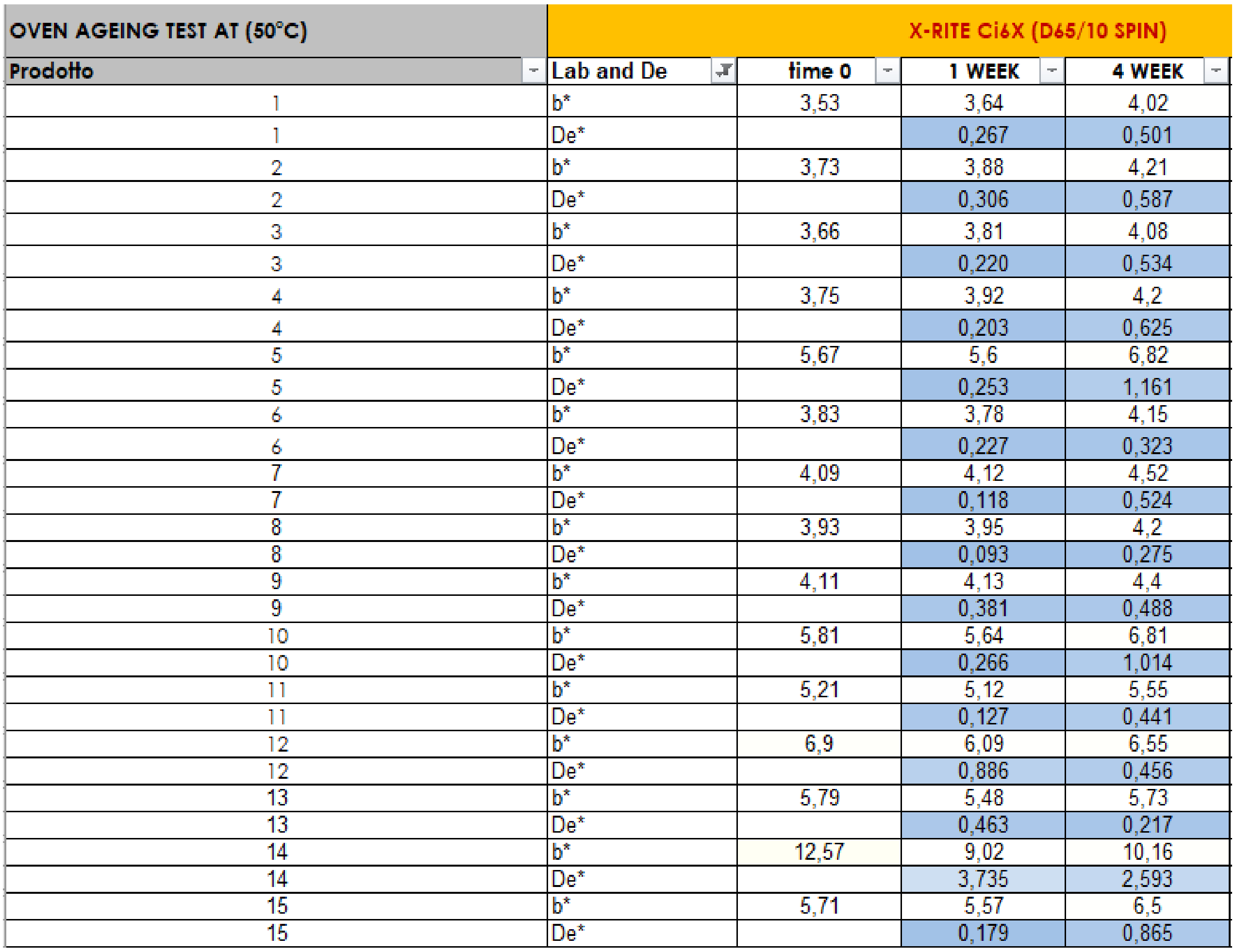


Fig 38; CIELAB SPHERE

16 probes of ageing tests were performed (Tab 2, Fig 39) , and hereafter the results are reported, with the Table reporting… while in the figure picture of the surface color is shown:



OVEN AGEING TEST AT (50°C)	**X-RITE Ci6X (D65/10 SPIN)**			
Prodotto	**Lab and De**	**time 0**	**1 WEEK**	**4 WEEK**
1	b*	3,53	3,64	4,02
1	De*		0,267	0,501
2	b*	3,73	3,88	4,21
2	De*		0,306	0,587
3	b*	3,66	3,81	4,08
3	De*		0,220	0,534
4	b*	3,75	3,92	4,2
4	De*		0,203	0,625
5	b*	5,67	5,6	6,82
5	De*		0,253	1,161
6	b*	3,83	3,78	4,15
6	De*		0,227	0,323
7	b*	4,09	4,12	4,52
7	De*		0,118	0,524
8	b*	3,93	3,95	4,2
8	De*		0,093	0,275
9	b*	4,11	4,13	4,4
9	De*		0,381	0,488
10	b*	5,81	5,64	6,81
10	De*		0,266	1,014
11	b*	5,21	5,12	5,55
11	De*		0,127	0,441
12	b*	6,9	6,09	6,55
12	De*		0,886	0,456
13	b*	5,79	5,48	5,73
13	De*		0,463	0,217
14	b*	12,57	9,02	10,16
14	De*		3,735	2,593
15	b*	5,71	5,57	6,5
15	De*		0,179	0,865

Tab 2: oven ageing tests Ca/Zn stabiliser results

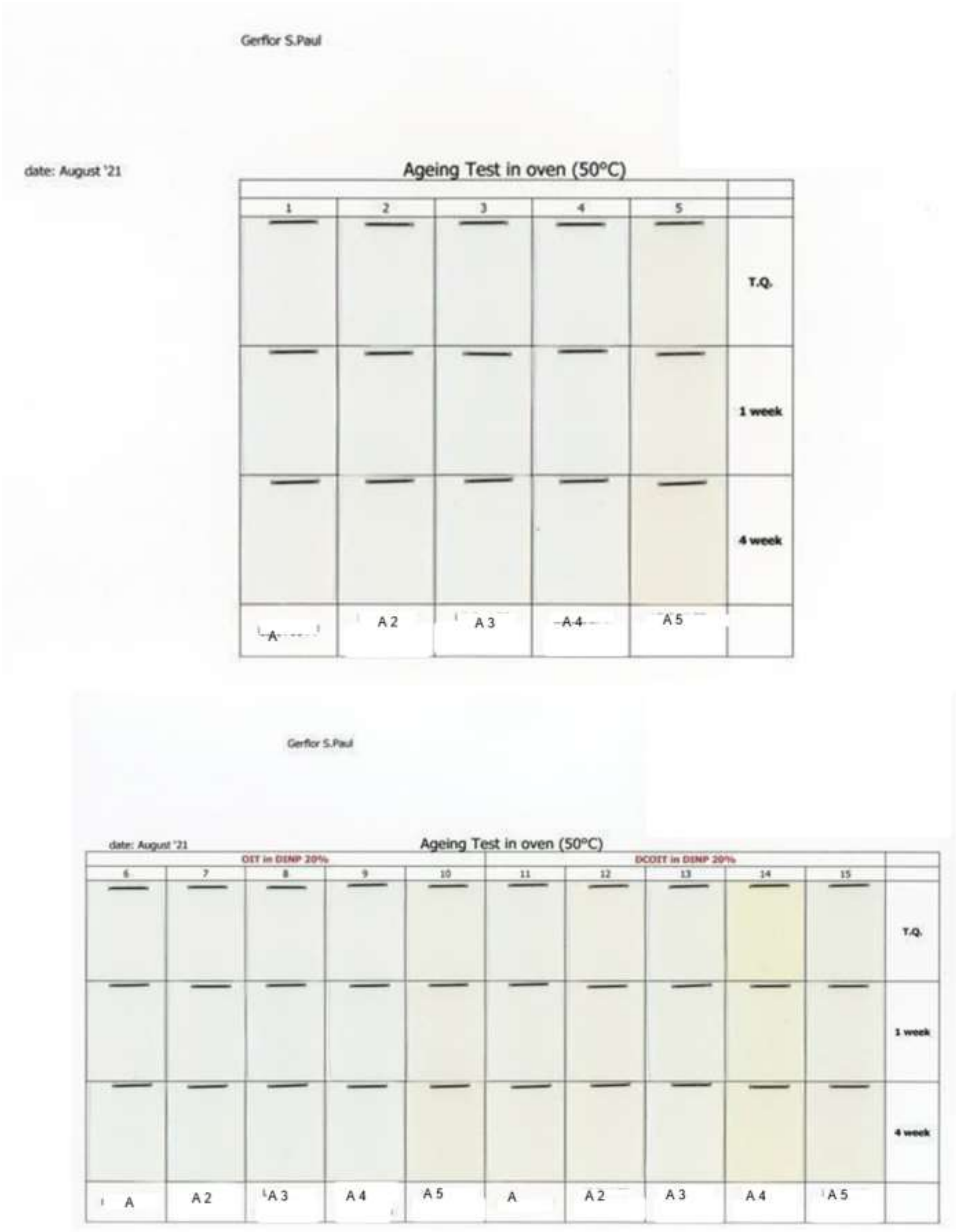


Fig 39: Ageing Tests of "A" stabilisers

The most interesting formulation is STAB A 3 (13th probes) that keeps the same yellow value during the whole test, but probably this is due more to the high Ca content than to the lack of reaction between

Phosphite and Biocide, and the formulations without the phosphite (5th, 10th, 15th probe). Conversely the STAB A 4 (14th probe) yellows already in the TQ foil corresponding to the first hours.

Alternative Ba/Zn stabiliser formulations were prepared (stab B, stab C).

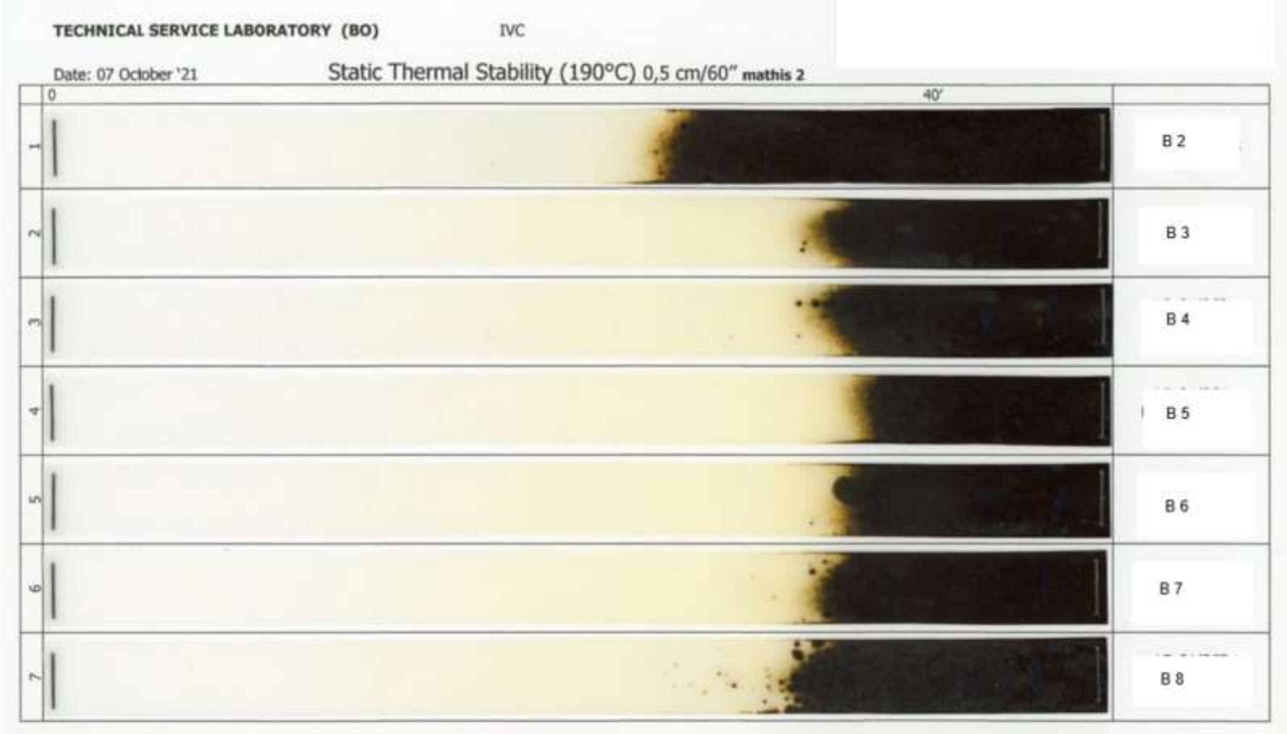
STAB B	grams	STAB C	grams
Zn Oxide	3.9	Zn Oxide	3.2
Versatic Acid	16.82	Versatic Acid	26.6
Benzoic Acid	1.98	Benzoic Acid	3
Toluic Acid	5.34	Oleic Acid	15.6
Oleic Acid	6.36	Barium Hydrated	13.3
Barium Hydrated	6.22	Arenox A 22	1
Oil Soybean	5.1	DBM	3.8
		Reaflexab/218	38

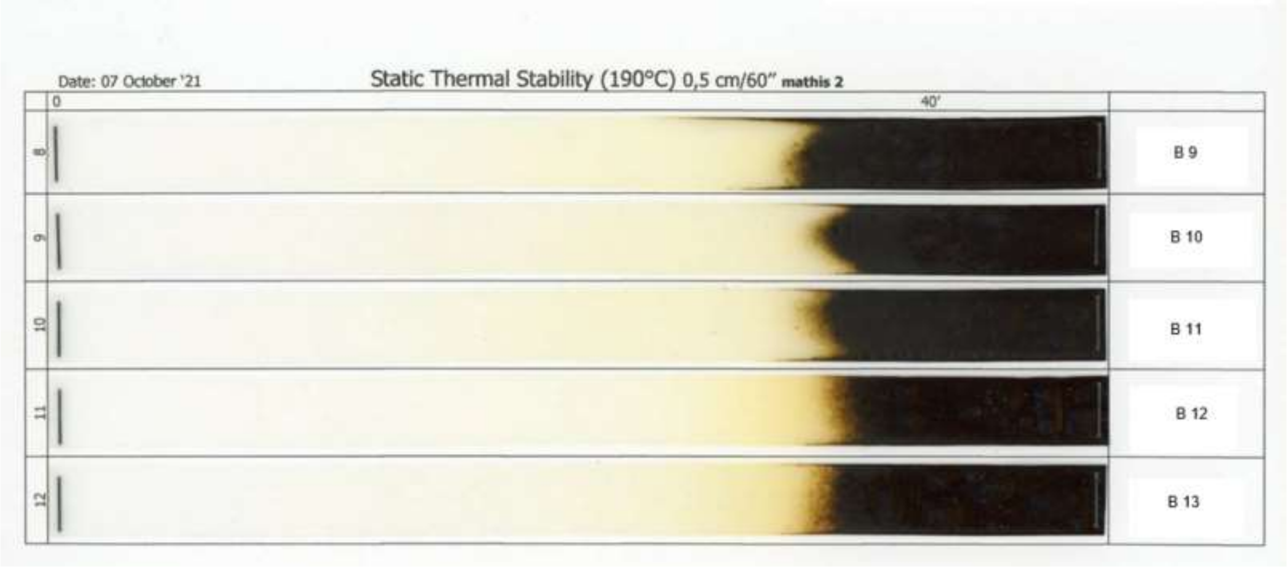
12 different variants of the Ba/Zn soap were prepared , in the series the type and the quantity of antioxidants (A 76, A 10 , A 22, BHT, HOX) are different, in some cases DHA “docosanoic acid” and DBM, “dibenzoil methane” (co-antioxidants) are added in order to evaluate the interaction with antioxidants and with the biocides.

STAB B 2	(no AO)
STAB B 3	(A/76)
STAB B 4	(A/76+DHA)
STAB B 5	(A/76X2)
STAB B 6	(A/10)
STAB B 7	(A/10+DHA)
STAB B 8	(A/10X 0,25)
STAB B 9	(A/22)
STAB B 10	(A/22X 0,35)
STAB B 11	(BHT)
STAB B 12	(HOX 3)
STAB B 13	(HOX 3X0,25)
STAB C 2 no phosphite	no AO)
STAB C 3 no phosphite	(A/22+DBM)
STAB C 4 no phosphite	(A/22+DHA)
STAB C 5 no phosphite	(A/22)
STAB C 6 no phosphite	(A/22X0,25+DHA)

STATIC THERMOSTABILITY TEST (Ba/Zn) (3.10)

Static thermostability tests (Fig 40) of Ba/Zn stabilisers in presence of DCOIT, OIT, or in the absence of the biocide are performed in a WERNER MATHIS thermostat.





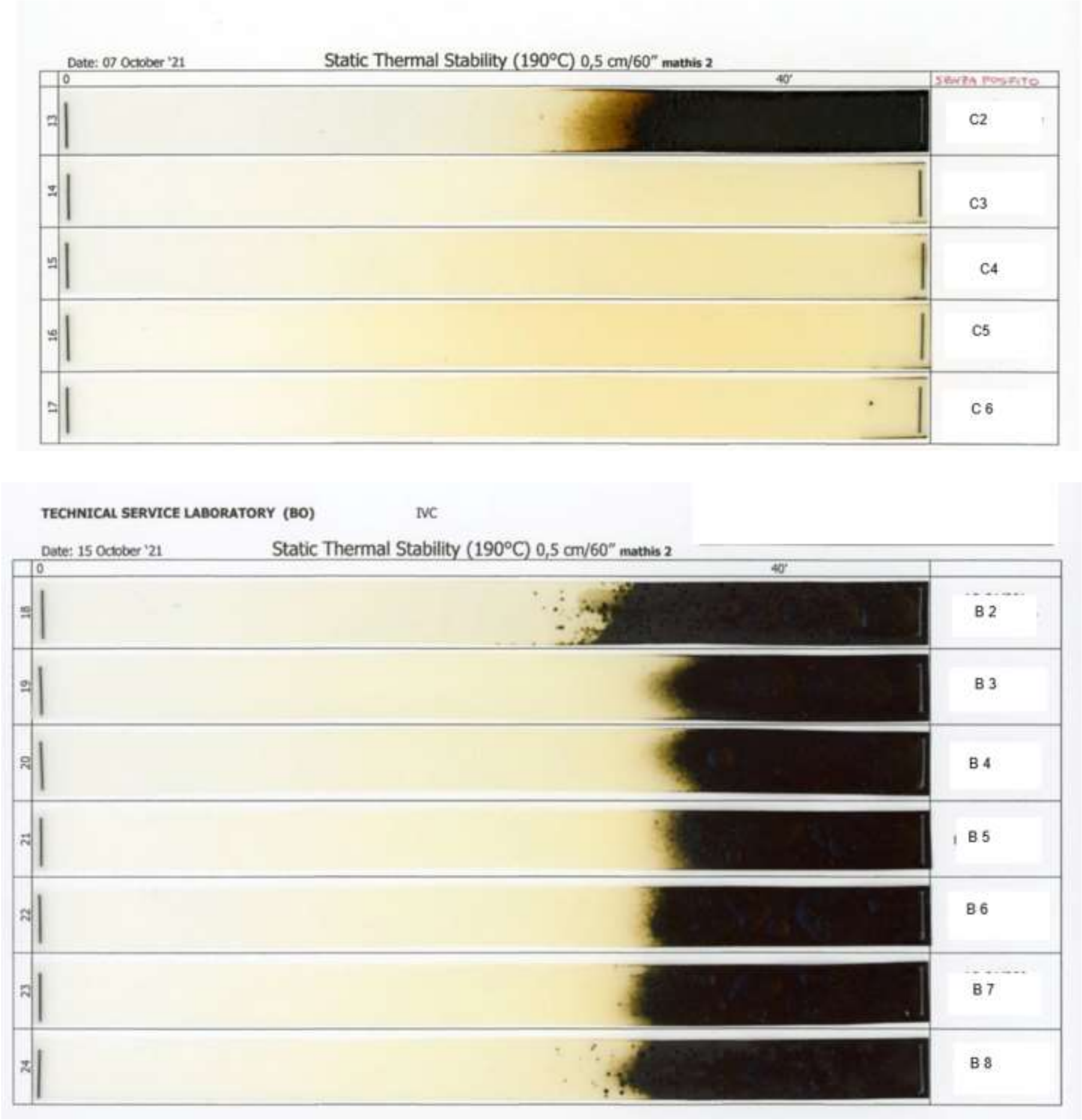
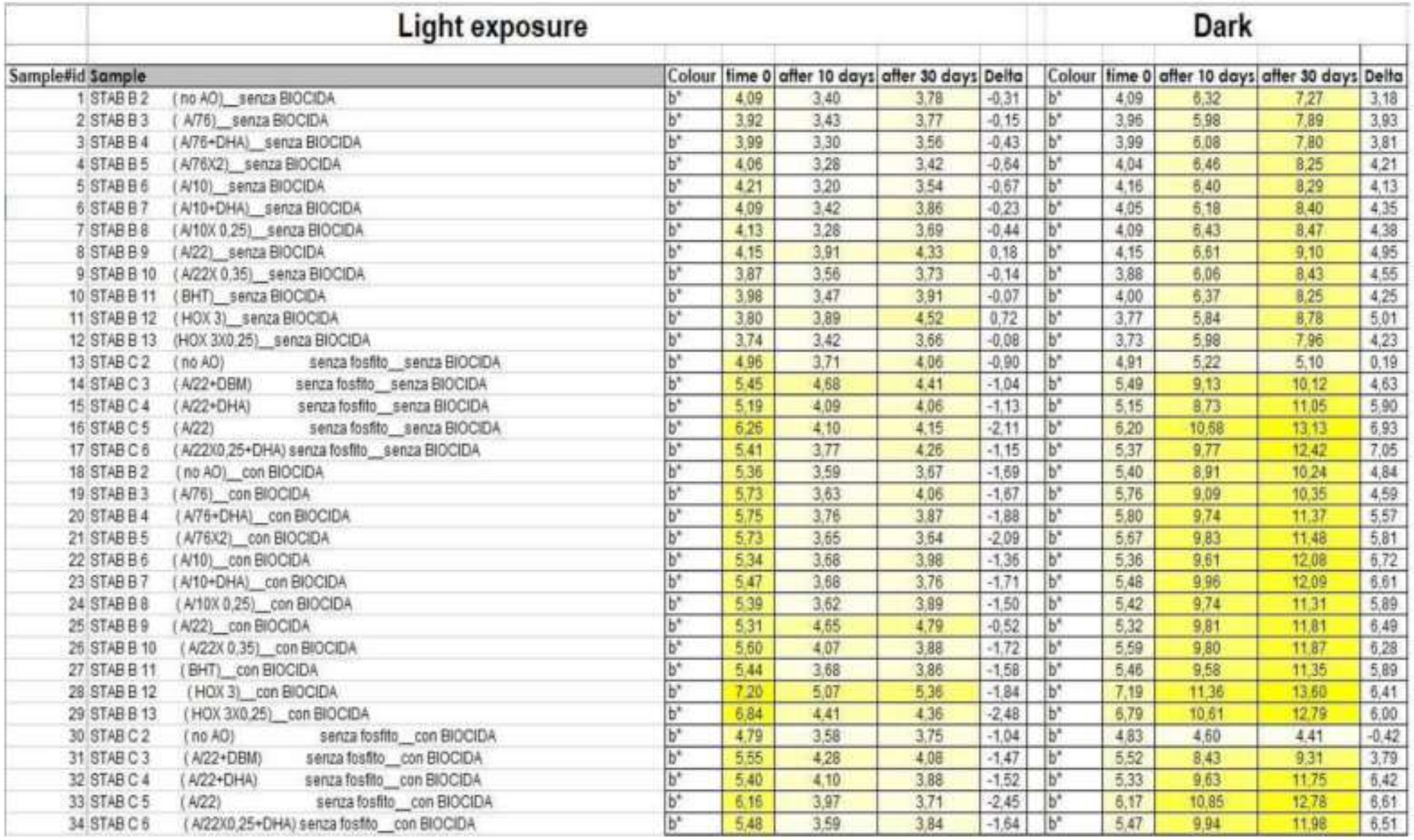


Fig 40. Ageing tests of B,C stabilisers (Ba/Zn)

“CARPET EFFECT” AGEING TESTS (3.11)

In order to simulate the effect of a covering (carpet, sofa, table) on the PVC flooring and on the Ba/Zn stabiliser, ageing tests in dark/light conditions were performed. A piece of the stabiliser after the MATHIS TEST was kept under lamp irradiation while a section was covered by a dark object. “De” parameter was evaluated. UV radiation can cause the degradation reaction to be reversible thus preserving the stabiliser and shifting the equilibrium (Fig 22), for this reason certain “b” values from the colorimetric assessment are observed to lower with time.



	Light exposure						Dark				
Sample#id	Sample	Colour	time 0	after 10 days	after 30 days	Delta	Colour	time 0	after 10 days	after 30 days	Delta
1	STAB B 2 (no AO)__senza BIOCIDA	b*	4,09	3,40	3,78	-0,31	b*	4,09	6,32	7,27	3,18
2	STAB B 3 (A/76)__senza BIOCIDA	b*	3,92	3,43	3,77	-0,15	b*	3,96	5,98	7,89	3,93
3	STAB B 4 (A/76+DHA)__senza BIOCIDA	b*	3,99	3,30	3,56	-0,43	b*	3,99	6,08	7,80	3,81
4	STAB B 5 (A/76X2)__senza BIOCIDA	b*	4,06	3,28	3,42	-0,64	b*	4,04	6,46	8,25	4,21
5	STAB B 6 (A/10)__senza BIOCIDA	b*	4,21	3,20	3,54	-0,67	b*	4,16	6,40	8,29	4,13
6	STAB B 7 (A/10+DHA)__senza BIOCIDA	b*	4,09	3,42	3,86	-0,23	b*	4,05	6,18	8,40	4,35
7	STAB B 8 (A/10X 0,25)__senza BIOCIDA	b*	4,13	3,28	3,69	-0,44	b*	4,09	6,43	8,47	4,38
8	STAB B 9 (A/22)__senza BIOCIDA	b*	4,15	3,91	4,33	0,18	b*	4,15	6,61	9,10	4,95
9	STAB B 10 (A/22X 0,35)__senza BIOCIDA	b*	3,87	3,56	3,73	-0,14	b*	3,88	6,06	8,43	4,55
10	STAB B 11 (BHT)__senza BIOCIDA	b*	3,98	3,47	3,91	-0,07	b*	4,00	6,37	8,25	4,25
11	STAB B 12 (HOX 3)__senza BIOCIDA	b*	3,80	3,89	4,52	0,72	b*	3,77	5,84	8,78	5,01
12	STAB B 13 (HOX 3X0,25)__senza BIOCIDA	b*	3,74	3,42	3,66	-0,08	b*	3,73	5,98	7,96	4,23
13	STAB C 2 (no AO) senza fosfito__senza BIOCIDA	b*	4,96	3,71	4,06	-0,90	b*	4,91	5,22	5,10	0,19
14	STAB C 3 (A/22+DBM) senza fosfito__senza BIOCIDA	b*	5,45	4,68	4,41	-1,04	b*	5,49	9,13	10,12	4,63
15	STAB C 4 (A/22+DHA) senza fosfito__senza BIOCIDA	b*	5,19	4,09	4,06	-1,13	b*	5,15	8,73	11,05	5,90
16	STAB C 5 (A/22) senza fosfito__senza BIOCIDA	b*	6,26	4,10	4,15	-2,11	b*	6,20	10,68	13,13	6,93
17	STAB C 6 (A/22X0,25+DHA) senza fosfito__senza BIOCIDA	b*	5,41	3,77	4,26	-1,15	b*	5,37	9,77	12,42	7,05
18	STAB B 2 (no AO)__con BIOCIDA	b*	5,36	3,59	3,67	-1,69	b*	5,40	8,91	10,24	4,84
19	STAB B 3 (A/76)__con BIOCIDA	b*	5,73	3,63	4,06	-1,67	b*	5,76	9,09	10,35	4,59
20	STAB B 4 (A/76+DHA)__con BIOCIDA	b*	5,75	3,76	3,87	-1,88	b*	5,80	9,74	11,37	5,57
21	STAB B 5 (A/76X2)__con BIOCIDA	b*	5,73	3,65	3,64	-2,09	b*	5,67	9,83	11,48	5,81
22	STAB B 6 (A/10)__con BIOCIDA	b*	5,34	3,68	3,98	-1,36	b*	5,36	9,61	12,08	6,72
23	STAB B 7 (A/10+DHA)__con BIOCIDA	b*	5,47	3,68	3,76	-1,71	b*	5,48	9,96	12,09	6,61
24	STAB B 8 (A/10X 0,25)__con BIOCIDA	b*	5,39	3,62	3,89	-1,50	b*	5,42	9,74	11,31	5,89
25	STAB B 9 (A/22)__con BIOCIDA	b*	5,31	4,65	4,79	-0,52	b*	5,32	9,81	11,81	6,49
26	STAB B 10 (A/22X 0,35)__con BIOCIDA	b*	5,60	4,07	3,88	-1,72	b*	5,59	9,80	11,87	6,28
27	STAB B 11 (BHT)__con BIOCIDA	b*	5,44	3,68	3,86	-1,58	b*	5,46	9,58	11,35	5,89
28	STAB B 12 (HOX 3)__con BIOCIDA	b*	7,20	5,07	5,36	-1,84	b*	7,19	11,36	13,60	6,41
29	STAB B 13 (HOX 3X0,25)__con BIOCIDA	b*	6,84	4,41	4,36	-2,48	b*	6,79	10,61	12,79	6,00
30	STAB C 2 (no AO) senza fosfito__con BIOCIDA	b*	4,79	3,58	3,75	-1,04	b*	4,83	4,60	4,41	-0,42
31	STAB C 3 (A/22+DBM) senza fosfito__con BIOCIDA	b*	5,55	4,28	4,08	-1,47	b*	5,52	8,43	9,31	3,79
32	STAB C 4 (A/22+DHA) senza fosfito__con BIOCIDA	b*	5,40	4,10	3,88	-1,52	b*	5,33	9,63	11,75	6,42
33	STAB C 5 (A/22) senza fosfito__con BIOCIDA	b*	6,16	3,97	3,71	-2,45	b*	6,17	10,85	12,78	6,61
34	STAB C 6 (A/22X0,25+DHA) senza fosfito__con BIOCIDA	b*	5,48	3,59	3,84	-1,64	b*	5,47	9,94	11,98	6,51

Fig 41: ageing tests result in dark and light conditions of B.C stabilisers

RESULTS OF AGEING TESTS Ba/Zn STABILISERS

STAB C 2 lacks the phosphite and antioxidant, it’s very powerful and in both conditions preserve the transparent color better than other formulations. It’s just a Ba/Zn soap that is very difficult to synthesize because the phosphite generally keeps standing the entire structure empeeding the precpitation of Ba/Ca salts.

CONCLUSIONS (4)

Aim of the work was to identify the components of a Ca/Zn liquid PVC stabiliser used in PVC flooring that interacted with the biocide DCOIT thus provoking the yellowing of the entire structure, and propose an alternative formulation of the stabiliser. With preliminary tests carried out on the top coat (IR tests, GC-MS and LC) it was highlighted that the phosphite undergoes a nucleophilic substitution on the isothiazolynic ring of the biocide. Consequently, modifications on both the traditional Ca/Zn and on a completely different Ba/Zn stabiliser were carried out. In particular thermostability and ageing tests was used to determine which of the new formulations maintained the transparent color for the longest time. Among the Ca/Zn liquid stabilisers the best were those without the phosphite or with a high level of Ca that seem to hamper the reaction between the phosphite and the DCOIT, changing on the extent of the antioxidants good results were obtained. Among the Ba/Zn the best formulation (STAB C 2) was a simple Ba/Zn soap without the phosphite and the antioxidant. It kept the transparency for an acceptable time and guaranteed high performance both in dark and in light presence (carpet effect). Problems of this innovative formulation were related to the absence of the phosphite that in general keeps standing the structure hampering the precipitation of Ba/Zn species that in this case are more probable, so further studies are necessary to achieve a high Ba title stabiliser very efficient in PVC flooring stabilisation.

EXPERIMENTAL PART (5)

-ISALCHEM 123 + DCOIT (5.1)

ISALCHEM 123 (Tb 261-298°C, density 0.863g/cm³) and DCOIT (solid 98% m/m) were added in CH2Cl2 (Tb 40 °C, density 1.33g/cm³). Temperature of reaction 50°C, p= 1 atm

Fig: reaction of DCOIT and ISALCHEM 123

After 5 h under vigorous agitation at 50°C the solution kept transparent, exaclty as the previous attempt where ISALCHEM 123 was added in excess, after one night at environmental T with no agitation the product crystallized and happeared like as a white solid suspended in alcoholic matrix.

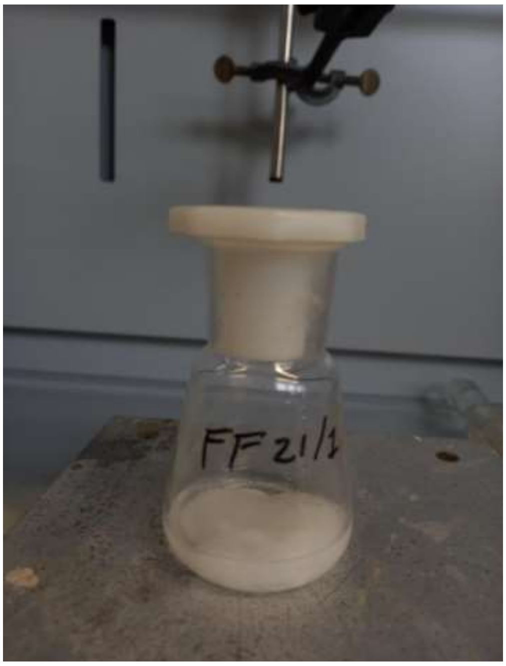


Fig 21 Reaction product of ISALCHEM 123 + DCOIT

-CHEL 704 + DCOIT (5.2)

5g of DCOIT and 13.46g of CHEL 704 were added to 40.96 ml of CH_2Cl_2. Temperature of reaction 60°C

-WESTON 619 + DCOIT (5.3)

5g of WESTON 619 (Tm 37-46°C) and 16g of CHEL 704 were added to 40.96 ml CH_2Cl_2. Temperature reaction was raised up to 60°C gradually.

Fig. 33 reaction product of WESTON 619 + DCOIT after 2

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