

Catalyst alternatives to replace DBTDL and crosslink speed improvement of a low voltage cable insulation

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ABSTRACT

In order to increase speed of silane crosslinking polyethylene, a catalyst is needed. The most common one is DBTDL (DiButyl Tin DiLaurate) which is classified as reprotoxic 1B, mutagenic 2 and toxic for specific target organs. For many years alternatives to DBTDL were investigated and studied in cable and other applications. A brief state of the art indicates that some catalysts were explored. Some catalysts as well as additional factors were studied to increase crosslinking speed. In the present paper the authors describe the development of low voltage (LV) insulation without CMR product where the speed of the crosslinking process has been improved.

KEYWORDS

CROSSLINKING – LOW VOLTAGE – INSULATION – CATALYST

I. INTRODUCTION

Crosslinked polyethylene is commonly used as insulation as it allows insulation to withstand 90°C in normal service conditions and 250°C in case of short-circuit. Among the three crosslinking methods (e-beam, peroxide and silane), silane crosslinking is the most used in low voltage cables as it associates a low cost, a good processability and a good efficiency. However, silane crosslinking polyethylene is very slow and needs a catalyst to increase crosslinking speed. The most common catalyst is DBTDL (DiButyl Tin DiLaurate) as it allows a good and quick crosslinking of polyethylene without damaging the other insulation properties.

However, in addition to be corrosive and very toxic to environment, DBTDL is classified as:

- Reprotoxic 1B (H360FD), that is to say, it may damage fertility and may damage the unborn child.
- Mutagenic 2 (H341), that is to say, it is suspected of causing genetic defects.
- Toxic for specific target organs (H370 & H372) after short and long term (or repeatable exposure).



One other demand of industry is to be able to crosslink insulation at ambient conditions without using a process to accelerate again the reaction (water bath or sauna). This study deals with the development of a formula without CMR catalyst, able to crosslink at ambient conditions. This solution was specially developed to comply with the French specification NF C 33-209 (overhead LV cables)

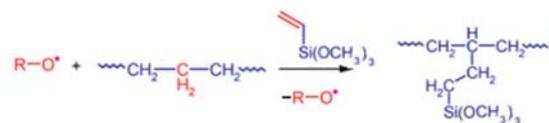
as the test method used to evaluate crosslinking is one of the most severe.

II. SILANE CROSSLINKING POLYETHYLENE

Silane crosslinking polyethylene is based on 3 reaction steps:

- 1) Vinylsilane grafting onto the polyethylene chains

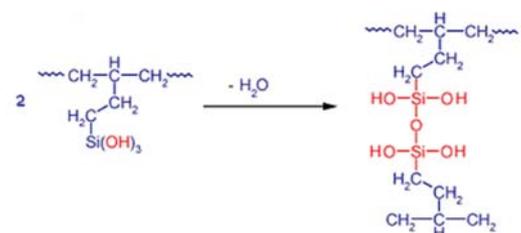
This reaction is initiated by the decomposition of peroxide, creating radicals. Then, radicals react with polyethylene molecules, allowing silane to graft onto polyethylene.



- 2) Hydrolysis of silane functions to silanol



- 3) Condensation of silanol groups to create siloxane bonds (three dimensional network)



III. HOW DO TIN-BASED CATALYSTS WORK

A catalyst is used to activate and speed up the 2nd and 3rd reaction steps. To be efficient, tin-based catalyst should:

- Have a good solubility in the hydrophobic polymer in order to facilitate its dispersion
- Contain polar groups in order to guarantee coordination of the alkoxy groups of silane and water first and silanol molecules secondly.

DBTDL associates the two previous properties thanks to its long hydrocarbon chains and its ester groups as described by K. Weissenbach and A. Ioannidis [1].

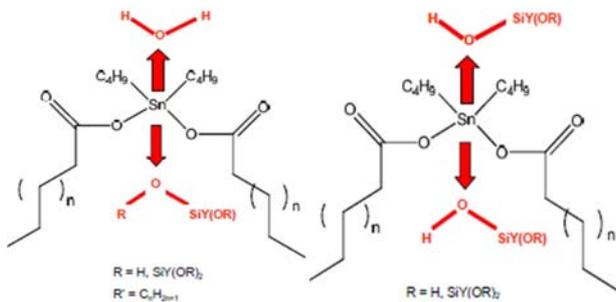


Figure 1: Proposed transition state for DBTDL as hydrolysis and condensation catalyst

IV. FACTORS ACCELERATING CROSSLINKING

Other factors can participate in speeding up crosslinking of silane grafted polyethylene among which some are listed below:

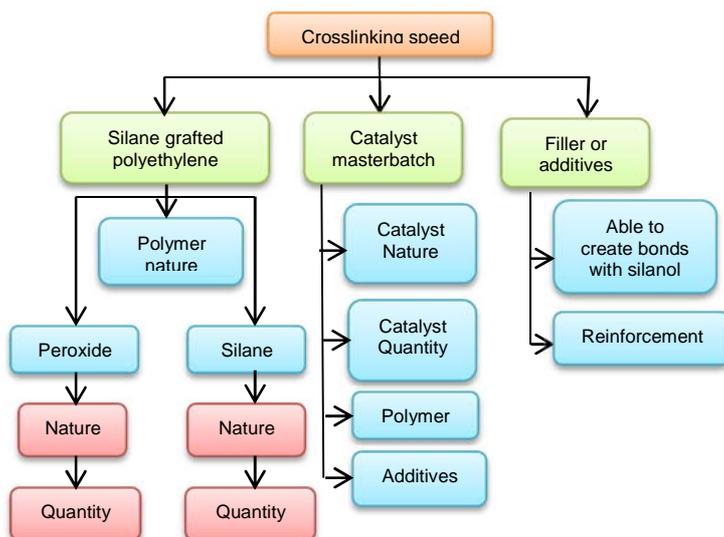


Figure 2: Factors influencing the speed of reactions

1) Silane grafted polyethylene

Crosslinking speed is directly linked to the concentration of reactive products meaning that the number of silane functions grafted on polyethylene, which is directly linked to:

- Silane percentage and nature (most preferred one is vinyltrimethoxysilane)
- Peroxide percentage and nature (most preferred one is dicumylperoxide)

Ratio of silane / peroxide is also a key factor to optimize silane grafting and avoid C-C bonds creation

- Polymer nature and so its ability to react with free radicals and to be grafted by silane molecules

2) Catalyst masterbatch

Indeed, catalyst molecule and its ratio have a huge impact on speed. Moreover, the melting points and melt flow index (MFI) of the masterbatch carrier are also important. In general, masterbatches disperse better in base polymers of equal or lower MFI. The melting point of the masterbatch should be lower than that of the base polymer to avoid imperfect melting with consequent poor dispersion. Furthermore, any additives helping dispersion of catalyst in polymer matrix can be used to improve its reactivity. Finally, addition of amorphous polymer in the catalyst masterbatch or as polymer matrix improve moisture permeability of insulation and then increase its reactivity.

3) Additives

Fillers can be used to reinforce polymer and get better properties at high temperature. Moreover, fillers or additives containing reactive groups able to create bonds with silanol groups, can participate to the three dimensional network and lead to a better crosslinking.

IV - STATE OF THE ARTS ABOUT CATALYSTS

Two categories of molecules can potentially work as silanol hydrolysis and condensation catalyst and are described in literature:

- 1) Acid (Lewis and Brønsted)
- 2) Base

1) Acid catalyst

a) Lewis acid

The most known are catalysts including carboxylates of metals, such as tin, zinc, iron, lead, copper, titanium and copper. According to metal used as well as molecules constructions, variable efficiencies are reported.

Examples of ones the most efficient are listed below ([2], [3], [4] and [5]):

	Classification	Level	Comparison with	Results	
				In water bath	At ambient conditions
DOTL (3648-18-8)	 STOT SE 2 (H371)	0.12%	DBTDL	21% higher HST with 0.02% more quantity	-
Copper(II) acetylacetonate (13395-16-9)	 H315; H319 ; H335	6.9 mmol/kg	Sulfonic acid	38% higher HST value with 3 times more quantity	-
Isopropyl triisostearoyl titanate (61417-49-0)	Not found	2.3 mmol/kg	DOTL	From 16 to 56% higher HST values	62% lower HST value
Butyl tin dihydroxide chloride (13355-96-9)	 H302 ; H312 ; H315 ; H319; H332 ; H335	0.8 to 2.4 mmol/kg	DBTDL	Up to 58% more gel content	Up to 23% more gel content

b) Brönsted acid

Sulfonic and carboxylic acids were recently studied to replace DBTDL as they have good reactivity and lead to less safety issue.

Examples of ones the most efficient are listed below ([6], [7], and [8]):

	Classification	Level	Comparison with	Results	
				In water bath	At ambient conditions
Stearic (57-11-4) and palmitic acid (57-10-3)	Not classified as dangerous	0.2 to 1.0%	DOTL	From 4 to 28% less gel content	-
Acetyl -p-dodecyl benzene sulphonate	Not found	0.8 mmol/kg	DBTDL & Sn(octoate)	From 17 to 47% higher gel content	From 40 to 114% higher gel content
4-Dodecylbenzene sulfonic acid (121-65-3)	 H314	1.5%	DBTDL & Sn(octoate)	From 17 to 41% higher gel content	From 33 to 103% more gel content
Dinonyl-naphthalene Disulfonic Acid (25322-17-2)	Not found	0.4 x 10 ⁻³ mM/g	DDBSA	Better HST values	Better HST values

2) Base

a) Hydroxide

Hydroxides of group 1 and 2 element of periodic Table of the Elements are proposed.

Examples of ones the most efficient are listed below ([9]):

	Classification	Level	Comparison with	Results	
				In water bath	At ambient conditions
KOH (1310-58-3)	 H290, H302, H314	2.3 mmol/kg	Sulfonic acid	-	50% less gel content
CsOH·H ₂ O (21351-79-1)	 H302, H314			-	13% less gel content

b) Amine

Examples of one of the most efficient are listed below ([10] and [11]):

	Classification	Level	Comparison with	Results	
				In water bath	At ambient conditions
N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexanediamine, polymer with 2,4,6-trichloro-1,3,5-triazene and 2,4,4-timethyl-1,2-pentanamine (70624-18-9)	Not found	0.45%	DBTDL	No result regarding crosslinking with 60 times more quantity	-
1,8-Diazabicyclo[5.4.0]undec-7-ene (6674-22-2)	  H290; H301; H314; H412	0.8-0.95%	Sulfonic acid	Same crosslinking with 30% more quantity and with another silane matrix (more silane content)	Same as in a water bath

Conclusion:

Several catalysts are reported to be good alternatives to DBTDL as they are not classified as mutagenic and reprotoxic. However, some of them are corrosive for metal or toxic for health and can't be considered as good alternatives to DBTDL. According to literature, the most promising ones are sulfonic and carboxylic acids as they match good efficiency and few hazards.

V. EXPERIMENTAL MEASUREMENT

1) Catalyst

Several catalysts were selected from the different categories describe previously by taking into account their potential activity and their classification.

Catalyst number	Nature	Classification
1	Di-sulfonic acid	Not classified as dangerous
2	Carboxylic acid	Not classified as dangerous
3	Carboxylic acid	Not classified as dangerous
4	Carboxylate of titanium	  H226 ; H319
5	Tin-based	 STOT SE 2 H371
6	Tin-based	 STOT SE 2 H371 H412
7	Amine	 H319

a) Masterbatches preparation

Each catalyst masterbatch was made by mixing a carrier polymer with antioxidant and catalyst (from 1.5 to 4%).

b) Visco-elastic couple measurement

• Method description

This method shows the crosslinking capability of a silanol condensation catalyst on a polyolefin having hydrolysable silane groups in presence of water.

Viscoelastic couple (S') of silane grafted polyethylene mixed with catalyst and water is measured at 200°C with a rheometer. The activity of the catalyst is directly linked to the increase of viscoelastic couple with time.

The maximum viscoelastic value (s' max) representing the maximum crosslinking which could be achieved with each catalyst is reported. The time to get 90% of the total crosslinking is also reported as T90.

Curves representing crosslinking got with DBTDL and without any catalyst are shown in the next graph.

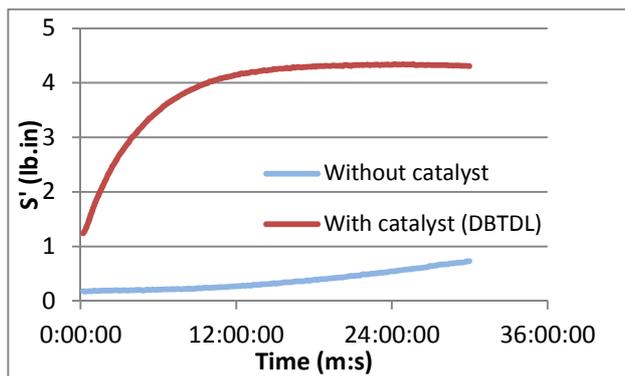


Figure 3: S' curves with and without catalyst

• Results

➔ Comparison of the 2 tin-based catalysts and DBTDL

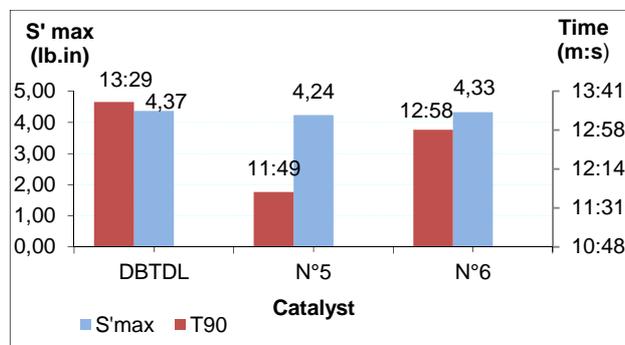


Figure 4: S' max and T90 of tin-based catalysts

Tin-based catalysts give similar results as DBTDL at the same concentration level.

➔ Comparison of tin-free catalysts and DBTDL

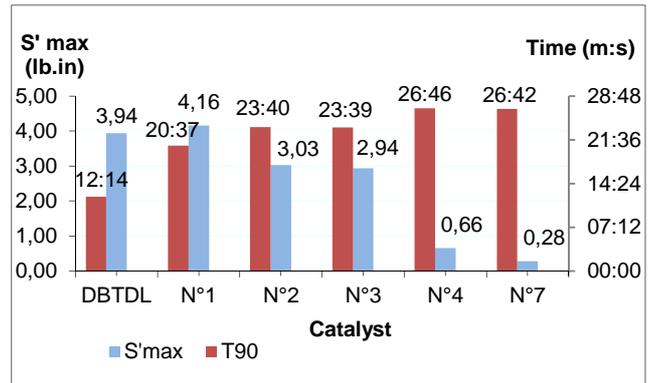


Figure 5: S' max and T90 of tin free catalysts

Catalyst n°1 gives a better S' max but a higher T90. So, it is able to create a better level of crosslinking but in a longer time. Catalysts n° 2 and 3 give lower S' max and higher T90. So, the level and the speed of crosslinking are lower. Catalysts n°4 and 7 give too much lower and slower crosslinking and can't be considered as good alternatives.

c) Extrusion and HST characterization

Formulas comprising the most promising catalysts, silane grafted polyethylene and carbon black were defined to get similar crosslinking level as the reference formula containing DBTDL. They were then extruded (thickness around 1.4-1.5 mm).

The formulas are described below:

Catalyst	Silane content of polyethylene (%)
DBTDL	0.9 - 1.1
N°1	1.1 - 1.3
N°2	1.7 - 1.9
N°3	1.7 - 1.9
N°5	0.9 - 1.1
N°6	0.9 - 1.1

The temperatures profile used is described below:

Z1	Z2	Z3	Z4	Head	Die
160	170	180	190	220	220

d) Hot Set Test (HST)

• Description

Hot Set Tests are performed according to IEC 60811-507 on dumb bell pieces.

Hot Set Tests were performed after curing samples in an 85°C water bath and after curing samples at ambient conditions (23°C and around 50% relative humidity).

Reference lines were marked 20 mm apart on dumb bells.

Each test pieces was fixed from upper end thereof in a support and the load of 0.3 MPa (according to NF C33-209 standard) are attached to the lower end of each test sample. After the oven temperature achieved again 200°C, test pieces are left 10 min more. Then, pre-marked lines were measured and the percentage hot set test elongation calculated. For permanent set percentage, the tensile force was removed from the test pieces and the pieces were then left 5 min before being removed and cool at room temperature. The permanent set percentage was calculated from the distance between marked lines. The average of two tests is calculated.

Specifications of the NF C 33-209 cables are:

Hot set test elongation ≤ 100% and permanent set ≤15%.

• Results

After 2, 4 and 6 hours in 85°C water bath

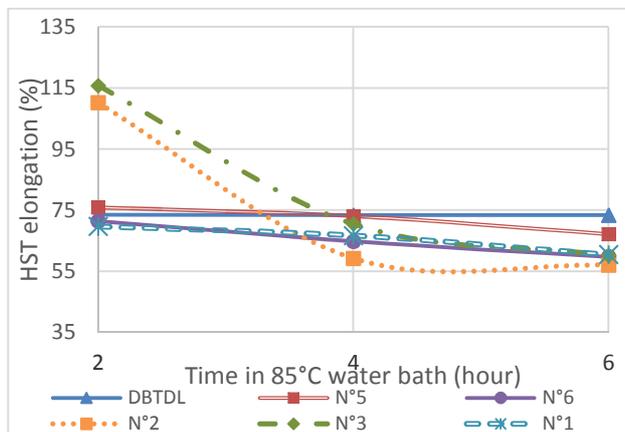


Figure 6: HST elongation after hours in 85°C water bath for each formula

After 2, 3 and 4 weeks at ambient conditions (23°C 50 relative humidity)

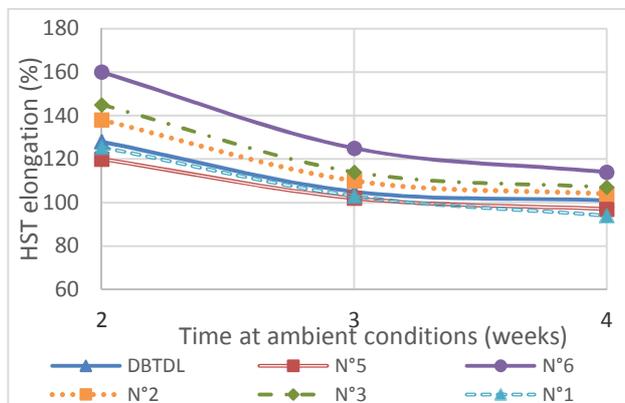


Figure 7: HST elongation after weeks at ambient conditions with the different catalysts

Catalysts n°1 and n°5 give similar results after crosslinking in 85°C water bath and at ambient conditions.

Catalysts n° 2 and 3 give slower crosslinking speed in water bath and at ambient conditions. Catalyst n°6 has a good efficiency if insulation is crosslinked in a water bath but not at ambient conditions.

2) Additional factors

a) Addition of fillers

Fillers and additives were added to formula containing catalyst n°1 and impact on crosslinking was assessed by measuring HST elongation values after 2 hours in 85°C water bath.

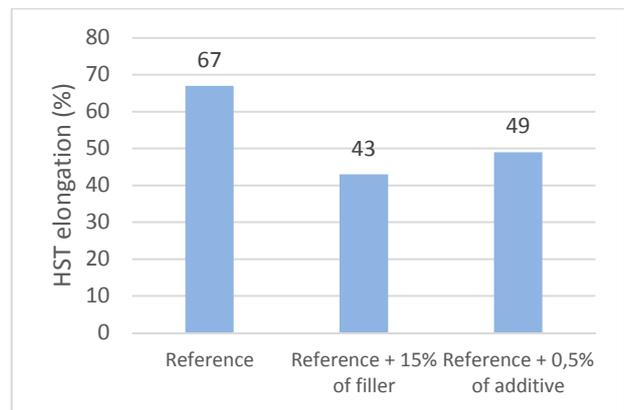


Figure 8: HST after crosslinking in water bath of formula containing fillers

Addition of fillers or additives improves HST elongation values.

b) Carrier of catalyst masterbatch

Two polymers having different characteristics were compared as carrier of catalyst masterbatch in the formula containing catalyst n°1 by measuring HST elongation values after crosslinking at ambient conditions.

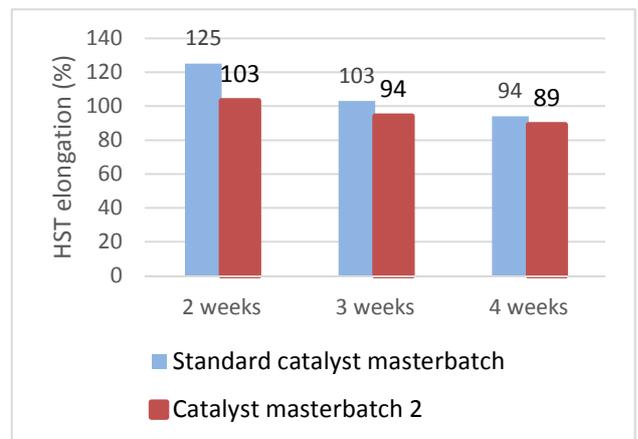


Figure 9: HST after weeks at ambient conditions with two carrier polymers

3) Optimized solution

Thanks to the previous studies, an optimized formula was developed containing:

- A silane grafted polyethylene containing about 1.9-2.3% of silane
- A catalyst masterbatch containing the catalyst n°1 made with an optimized polymer carrier
- Fillers and additives

a) HST measurement

HST values were measured after several weeks at ambient conditions.

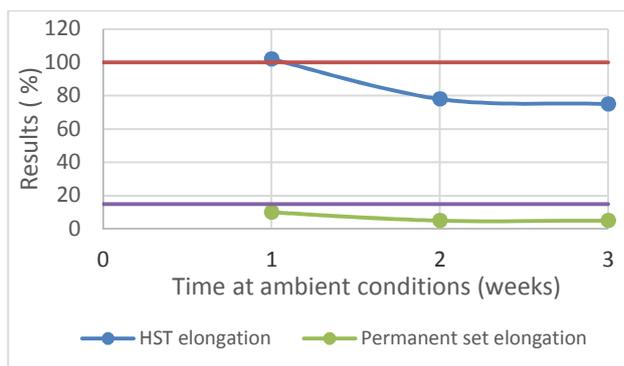


Figure 10: HST of the developed formula after 2 and 3 weeks at ambient conditions

b) Mechanical characteristics before and after 10 days aging at 150°C

• Method description

Aging and mechanical tests were performed (respectively) according to the standards IEC 60811-401 and IEC 60811-501. Test pieces are taken to be aged 10 days at 150°C.

5 dumb bell pieces having a thickness between 0.8 and 2 mm were prepared and mechanical characteristics were measured at 25 mm/min. Tensile strength (TS) and elongation at break (EB) were recorded. Variations of mechanical characteristics before and after aging were calculated.

• Results

	Before aging		After aging	
	TS (Mpa)	EB (%)	Δ TS (%)	Δ EB (%)
Specification	≥ 14.5	≥ 200	± 25	± 25
Results	15.4	350	+15	-17

CONCLUSION

By chosen the best combination of parameters (silane grafted polyethylene, catalyst masterbatch and additives), an optimized solution was developed.

This new solution combines mutually low safety risks as the catalyst chosen is not classified as dangerous with a better reactivity while crosslinking at ambient conditions between one and two weeks.

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GLOSSARY

DBTDL: DiButylTin Dilaurate

HST: Hot Set Test

LV: Low Voltage

TS: Tensile Strength

EB: Elongation at Break