RECENT ADVANCES IN PVC STABILITY WITH METAL AND ORGANIC COMPOUNDS

Alain Michel and Tran Van Hoang

CNRS - Laboratoire des Matériaux Organiques, BP 24, 69390 Vernaison, FRANCE

Abstract - The functions of the combinations of Zn-Ca and Cd-Ba soaps as primary stabilisers and various organic compounds as secondary stabilisers (epoxidised soya bean oil, phosphites, α-phenylindole, β-aminocrotonate esters, β-diketone and polyols) in the thermal stabilisation of the polyvinylchloride are reviewed through the mechanisms established previously. The use of chlorohexene isomers as models of allylic chlorine atoms located at the end of a growing polyene chain in the polymer has elucidated the basic chemistry of the reactions of stabilisation. Coulometric titration of metal chlorides accumulation in the polymer matrix has proved to be a powerful tool in the study of stabilisers transformation and in the true explanation of the synergistic action of the secondary stabilisers.

INTRODUCTION

Whatever is the role of the structural irregularities of polyvinyl chloride (PVC) such as allylic and tertiary chlorine atoms, head to head structures, carbonyl group and peroxides as initiation sites, the usual processing operations are able to cause chains scission and oxidation through radical mechanisms which can contribute to the polymer dehydrochlorination and allylic chlorine atoms generation. The dehydrochlorination reaction is accelerated by HCl itself. Otherwise whatever are the efforts to exterminate reactive centres through chemical pretreatment there remains a tendency for PVC to degrade thermally. At last as the PVC is a semi-crystalline polymer and as it never completely melted whatever are the processing operations (rolling mill, extrusion, injection) there is no doubt that the distribution of stabilisers is not uniform and mainly during the gelation phase. Thus the thermal degradation of the PVC during the processing operations remains the main problem because the zip dehydrochlorination causes discoloration and crosslinking of the polymer. Consequently the role of a stabilizer is not limited to removal of primary initiating sites (preventive function). Its main function is to substitute allylic chlorine atoms wherever they are generated during the processing operations by mechanochemical or oxidative means (curative function).

Four main classes of stabilisers are generally used and based respectively upon :

- lead compounds (sulfate, carboxylate, phosphite)
- tin compounds (di-alkyltin carboxylates, di-alkyl tin-di-thioglycolates)
- barium-cadmium soaps combination
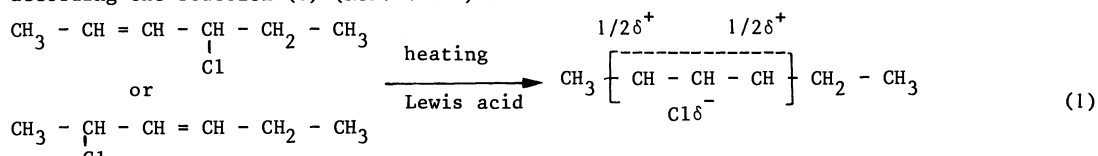- calcium-zinc soaps combination

The stabilisation recipes generally include the previous organo-metallic compounds as primary stabilisers and organic compounds as secondary stabilisers such as epoxidized soya bean oil, β-aminocrotonate esters, α-phenylindole, alkyl- aryl-phosphite, polyols, β-diketone...).

The purpose of this paper is to summarize the present states of our knowledge of the mechanism of thermal stabilisation of the polyvinylchloride using the previous organo-metallic and organic compounds as stabilisers. Nevertheless as our own work has been limited mainly to the study of the calcium-zinc combination in presence or not of organic compounds and to the study of tin compounds the emphasis will be on these two classes of stabilisers.
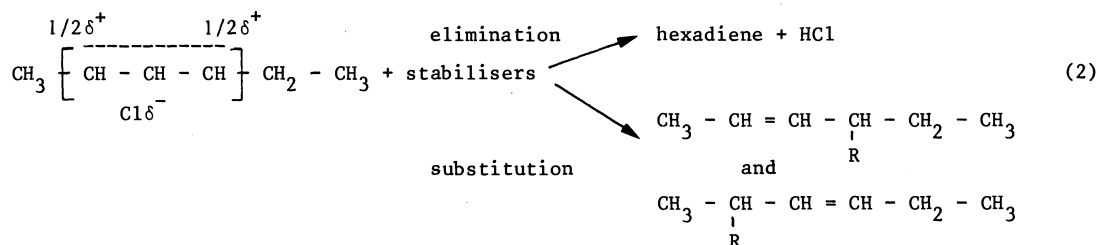
METHODOLOGY OF RECENT RESEARCH

From a chemical point of view a better understanding of the mechanisms of action of the stabilisers comes from the basic studies of their reaction with model compounds of PVC labile chlorine atoms. Because the main function of a stabiliser is to stop a soon as possible the propagation of the zip-dehydrochlorination by reaction with the allylic chlorine atoms located at the end of a growing polyene chain, the chlorohexene is a suitable model to explain some aspects of PVC stabilisation. In our studies this compound is generally an equimolar mixture of the two isomers 4-chlorohex-2-ene and 2-chlorohex-3-ene the composition depending on the method of preparation (Ref. 1, 2 & 3).

By heating or in presence of a Lewis acid these two isomers give the same allylic carbocation according the reaction (1) (Ref. 4 & 5) :

$$CH_3 - CH = CH - \underset{\underset{Cl}{|}}{CH} - CH_2 - CH_3$$

or

$$CH_3 - \underset{\underset{Cl}{|}}{CH} - CH = CH - CH_2 - CH_3$$

$$\xrightarrow[\text{Lewis acid}]{\text{heating}}$$

$$CH_3 \overset{1/2\delta^+ \qquad 1/2\delta^+}{\left[\underset{Cl\delta^-}{CH - CH - CH} \right]} CH_2 - CH_3 \qquad (1)$$

From the carbocation in presence of a stabiliser there are two competitive reactions according the next scheme (2) :

$$CH_3 \overset{1/2\delta^+ \qquad 1/2\delta^+}{\left[\underset{Cl\delta^-}{CH - CH - CH} \right]} CH_2 - CH_3 + \text{stabilisers} \Big\langle$$

elimination → hexadiene + HCl

substitution and

$$CH_3 - CH = CH - \underset{\underset{R}{|}}{CH} - CH_2 - CH_3$$

$$CH_3 - CH - CH = CH - CH_2 - CH_3$$
(with R)

(2)

Hexadiene formation pictures the PVC degradation and the substitution reaction pictures the stabilisation reaction of the polymer and gives informations on the efficiency of the stabiliser.

The experiments are carried out in solution and the two competitive reactions can be followed kinetically through gas chromatography analysis to get the total transformation of the chlorohexene, the hexadiene and the products of substitution.

The problem then arises to correlate the results obtained from the model compound to the polymer. Torque measurement using the Brabender plasticorder is a mean of following the effect of the stabilisers and their by-products on the polymer during the processing operations (Ref. 6). The torque first increases up to a first maximum because of the gelation. Then it decreases to a plateau value at a level depending on the molecular weight of the polymer and the efficiency of the lubricant system. When most of the stabilisers has been consumed the torque increases again because of the crosslinking of the polymer. The time T_A between the gelation peak and the cross-linking peak is called the action time of the stabiliser system. It takes into account the main role of the stabilisers and their by-products (crosslinking rate).
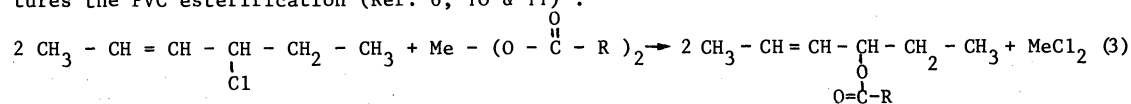
Otherwise a better knowledge of the role of the stabilisers during the PVC processing comes from the use of new analytical methods developped for the titration of the stabilisers or their by-products in the polymer matrix (Ref. 7). The coulometric titration of chloride ions has proved to be a powerful tool in this respect and mainly to understand the mechanisms of synergism between the metal soaps and the organic compounds as secondray stabilisers. It has been also a tool to verify the theory of the synergistic action in the combination of zinc-calcium or cadmium-barium soaps.

The organic part of the metal soaps may lead to either an ester group grafted onto the polymer through allylic chlorine atoms substitution or a carboxylic acid through HCl reaction. Carboxylic acid as stearic acid may be titrated in the polymer matrix using a potentiometric method (Ref. 7).

In some cases a combination of Gel Permeation Chromatography (GPC) with specific detectors (a refractometer which is sensitive to both polymer and organic-compound and a UV detector which is sensitive to the organic compound only) can be used to follow the grafting of the organic compound such as α-phenylindole (Ref. 8) or β-diketones (Ref. 9) onto the polymer.

THE MECHANISMS OF ACTION OF ZINC AND CADMIUM SOAPS AS PRIMARY STABILISERS

It is well established that metal soaps with a high ionization potential such as zinc and cadmium soaps react with the allylic chlorine atoms according to the reaction (3) which pictures the PVC esterification (Ref. 6, 10 & 11) :

$$2\ CH_3 - CH = CH - \underset{\underset{Cl}{|}}{CH} - CH_2 - CH_3 + Me - (O - \overset{\overset{O}{||}}{C} - R)_2 \rightarrow 2\ CH_3 - CH = CH - \underset{\underset{O}{|}}{CH} - CH_2 - CH_3 + MeCl_2 \quad (3)$$
$$(O=C-R)$$

Thus $ZnCl_2$ or $CdCl_2$ are by-products of the stabilisation reaction. As strong Lewis acid, they are powerful catalyst of the substitution reaction as well as the dehydrochlorination without presence of a nucleophilic reagent. Their accumulation in the polymer matrix has a deleterious effect on PVC thermal stability and they cause simultaneously the catastrophic blackening and
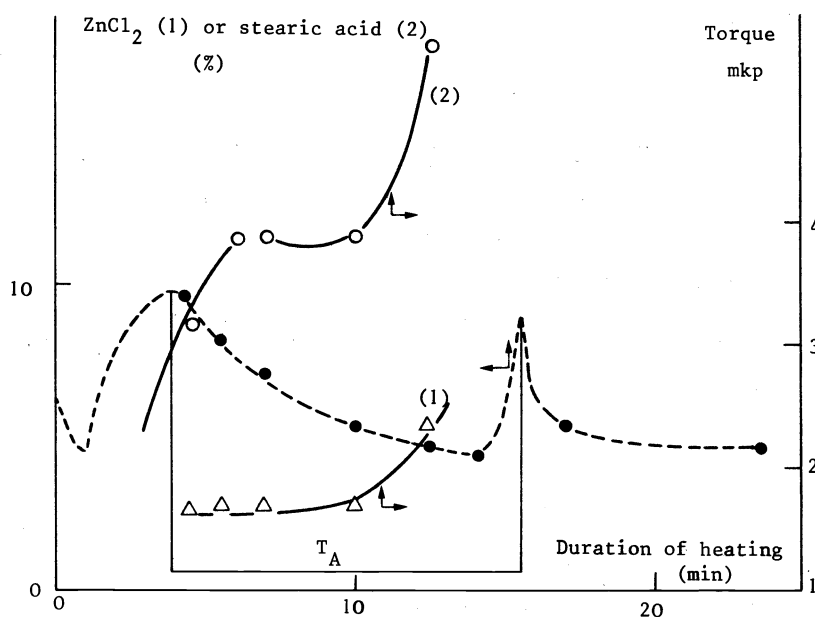
crosslinking of the polymer (Fig. 1).

Fig. 1. Zinc chloride and stearic acid accumulation in PVC during heating in the Brabender plasticorder at 190°C (●) plastogram PVC (100 phr), DOP (30 phr), zinc stearate (6.66 phr)

When zinc or cadmium stearates are used as stabilisers the stearic acid parallels chlorides formation and the consumption of stearates. It seems that after about 10 % of stabiliser transformation, the remaining stabiliser acts mainly as an HCl acceptor. This finding is similar to the results obtained by Vymazal (Ref. 12) who followed the consumption of cadmium stearate in the polymer matrix using IR spectroscopy. This result is unexpected and this behaviour has an explanation through the role of HCl. The previous stabilisation reaction through the O-alkylation is not permanent because the unsaturated ester is able to react with HCl even at moderate temperature to generate again allylic chlorine atoms and carboxylic acid (Ref. 6). Thus because the PVC is not totally melted at the usual temperatures of the processing operations, microdomains are not easily penetrated by the stabilisers and HCl eliminated from the inside of these unstabilised domains diffuses through the bulk of the polymer and reacts with the unreacted metal soaps and the grafted ester groups. The labile structures so produced in the stabilised PVC become again new sites for initiation of the dehydrochlorination. This behaviour contributes to the accelerated consumption of the metal soaps and is the true explanation for the sudden blackening of the polymer observed in practice after most of the stabiliser has been consumed.

Furthermore from the studies with model compound it has been shown that hexadiene undergoes the oligomerisation through a cationic polymerisation initiated by $ZnCl_3^-H^+$ ion pair (Ref. 6). This reaction pictures the PVC crosslinking when free $ZnCl_2$ is accumulated in the polymer matrix.

The strong activity of $ZnCl_2$ or $CdCl_2$ in the dehydrochlorination and crosslinking of the PVC suggests that it is necessary to delay their accumulation in the polymer matrix to improve the long-term stability of the polymer. The basis of the synergistic actions of the co-stabilisers (organometallic or organic compounds) will be to prevent the deleterious effect of these chlorides without interfering with the substitution reaction of the labile chlorine atoms and at last to delay their accumulation during the processing operations.

THE MECHANISM OF ACTION OF CALCIUM AND BARIUM SOAPS IN THE COMBINATION ZINC-CALCIUM AND CADMIUM-BARIUM SOAPS

Without a strong Lewis acid as $ZnCl_2$ or $CdCl_2$, calcium and barium soaps do not esterify the chlorohexene (Ref. 6). This result suggests that these stabilisers act only as HCl acceptors. Coulometric titration of $CaCl_2$ and stearic acid titration carried out in the polymer after heating in static or in dynamic conditions confirm this view (Ref. 13). Their amount although not exactly the same, is proportional to the heating time and increases on a parallel way. The accumulation of $CaCl_2$ in the polymer matrix has no deleterious effect on the blackening and the crosslinking of the polymer.

In presence of $ZnCl_2$, calcium stearate reacts with allylic chlorine atoms through the formation of the allylic carbo-cation as rate determining step from a kinetic point of view (Ref. 6) and as observed in the esterification of the chlorohexene by zinc stearate. The exchange reaction between zinc chloride and calcium soaps restores the active zinc soaps according to the reaction (4) :

$$ZnCl_2 + Ca - (O - \overset{O}{\overset{\|}{C}} - R)_2 \rightleftarrows CaCl_2 + Zn - (O - \overset{O}{\overset{\|}{C}} - R)_2 \qquad (4)$$
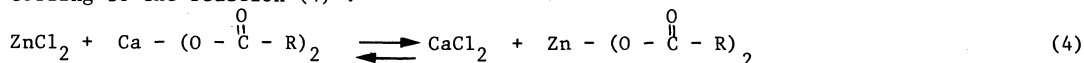
This exchange reaction has proved to be reversible and equilibrated (Ref. 6).

Otherwise the coulometric titration of the chlorides during the processing of the PVC in the Brabender plasticorder confirms the existence of the exchange-reaction between $ZnCl_2$ and calcium soaps because the increase of the chlorides in the polymer matrix does not cause the blackening and crosslinking of the polymer as it is observed if only zinc stearate is used as stabiliser. This finding suggests that the chlorides which are formed in a first time during the processing are mainly $CaCl_2$. In consequence the main role of the calcium soaps is to delay the accumulation of the zinc chlorides in the polymer matrix and to serve as a reserve to increase the lifetime of the zinc carboxylates. Nevertheless stearic acid and chlorides increase on a parallel way that suggests the combination of Zn-Ca soaps act mainly as an HCl acceptor.

The synergistic action in the combination of Zn-Ca soaps has also a complementary explanation on the basis of the formation of complexes between zinc soaps and calcium soaps (2 Zn, 1 Ca) as suggested by Onozuka (Ref. 10) and supported by the study of the infrared spectra of the equimolar mixture of the zinc and calcium stearate dispersed in the PVC. The carbonyl group of zinc stearate absorbs at 1540 cm^{-1} while calcium stearate gives two bands at 1540 and 1578 cm^{-1}. The mixture of the two carboxylates in PVC matrix shows only one large band at 1570 cm^{-1}. It was suggested that this complex prevent a rapid substitution of allylic chlorine atoms but its axact role in the stabilisation mechanism has not been clearly demonstrated. From our studies the existence of other complexes with the same stoechiometry (2 Zn, 1 Ca) between zinc chloride and calcium stearate or between zinc chloride and calcium chloride has been proved (Ref. 6 & 8). Such complexes may contribute to the inhibition of the catalytic activity of $ZnCl_2$ with respect to the dehydrochlorination of the PVC but also with respect to the substitution reaction of the allylic chlorine atoms. Nevertheless from our studies with model compound the synergistic action of the combination of calcium stearate with zinc stearate is most effective in decreasing the rate of the elimination reaction. With a molar Ca/Zn ratio larger than one the substitution reaction of allylic chlorine atoms is favoured compared with the elimination of HCl. When this ratio reaches the value of five the elimination reaction disappears totally although the substitution reaction takes place but with a reduced rate. It is interesting to note that the polymer blackening appears less suddenly as the Ca/Zn ratio increases. However during the processing of the PVC a yellow colour appears when this ratio is larger than one. This behaviour is to compare with the decrease of the esterification rate when the Ca/Zn ratio increases and is larger than one.

As other consequences of the synergistic effect when the ratio Ca/Zn increases, the time of action "T_A" of the stabiliser system increases and the rate of crosslinking decreases (Ref. 6). It is interesting to note that the dependence of T_A upon the ratio Ca/Zn is closely similar to that of the reduction of the elimination reaction in the model compounds. It is interesting to note also that the rate of the crosslinking process begins to decrease when the ratio Ca/Zn is higher than 2, value which corresponds to the amount of calcium compound necessary to engage all the $ZnCl_2$ in complexes.

These findings show the close parallelism between the action of the stabilisers with the chlorohexene as model of allylic chlorine atoms and their action in the polymer during the processing operations.

THE MECHANISM OF SYNERGISM BETWEEN METAL SOAPS AS PRIMARY STABILISERS AND ORGANIC COMPOUNDS AS SECONDARY STABILISERS

From the previous studies during the processing operations of the PVC in the presence of the combination of zinc - calcium soaps, there is accumulation of calcium and zinc chlorides in the polymer matrix. As a general rule the synergistic action of the secondary stabilisers is based upon their influence on the initial discoloration at the begining of the processing operations and their influence on the blackening time of the polymer.

The different functions of the short-term and long-term secondary stabilisers have been clarified using model compound of allylic chlorine atoms (chlorohexene) and coulometric titration of the chlorides to follow their influence on the accumulation of the $ZnCl_2$ and the $CaCl_2$ in the polymer matrix during the processing operations carried out on a rolling mill at 180°C. In this study a basic recipe was prepared using 1.6 phr of calcium stearate and 1.66 phr of zinc stearate. $5.18.10^{-3}$ mole of each organic compound were added either epoxidised soya bean oil, phosphites, α-phenylindole, benzoyl acetone and sorbitol. Samples were ta-

ken at three-minute intervals. The results are expressed as the percentage of chlorine libe-
rated with respect to complete transformation of stearates into chlorides versus time (Fig. 2).
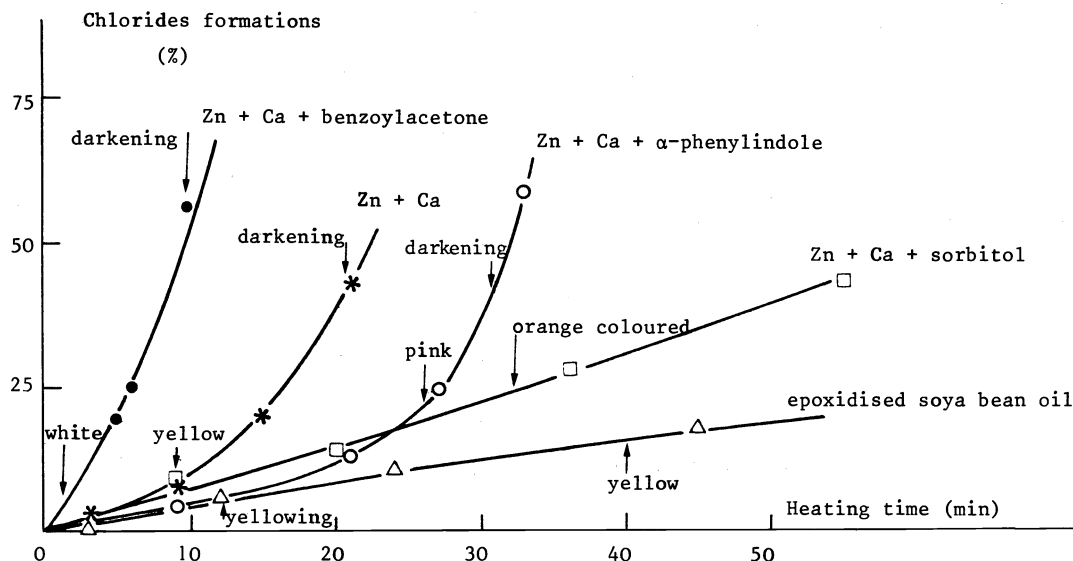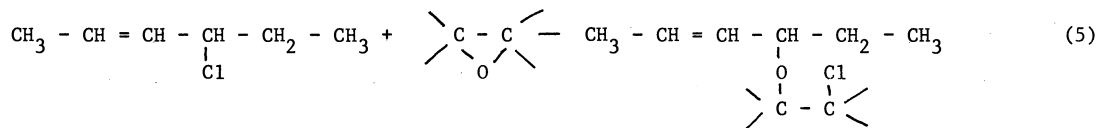

Fig. 2. Chlorides formation during during PVC processing at 180°C on rolling-mill.
(✱) Basic recipe (PVC Rhône-Poulenc Polymères RS 8000, 100 g ; calcium stearate,
1.60 phr ; zinc stearate, 1.66 phr). (○) Basic recipe and α-phenylindole,1.02 phr.
(△) Basic recipe and epoxidised soya bean oil, 6.6 phr). (□) Basic recipe and
sorbitol, 0.96 phr. (●) Basic recipe and benzoylacetone, 0.86 phr.

Without secondary stabilisers the yellow colour appears at about 10 % chloride yield and com-
plete blackening is observed at about 50 % yield.

Epoxidised soya bean oil. Chloride accumulation is strongly delayed and in consequence the
blackening of the polymer is retarded although discoloration (yellow then orange) may be ob-
served at low chloride level. Clearly for that reason the epoxy compounds are long-term sta-
bilisers.

Model compound studies have shown that in addition to the reaction with HCl which leads to
chlorhydrine formation, epoxidised compounds react with allylic chlorine atoms through an
O-alkylation according to the reaction (5) (Ref. 11-14).

$$CH_3 - CH = CH - \underset{\underset{Cl}{|}}{CH} - CH_2 - CH_3 + \overset{}{\underset{}{\overset{\diagdown}{\diagup} C - C \overset{\diagup}{\underset{O}{\diagdown}}}} \longrightarrow CH_3 - CH = CH - \underset{\underset{\underset{\diagup}{\overset{|}{\underset{}{C}} - \overset{Cl}{\underset{}{C}}}}{\overset{O}{|}}}{CH} - CH_2 - CH_3 \tag{5}$$

As for the hexenyl ester the allylic chlorinated ether produced through the O-alkylation re-
mains a weak structure and reacts with HCl to restore the initial allylic chlorine atom and
leads finally to hexadiene when an excess of chlorohexene is present with respect to the
stoechiometry of the reaction   (5)   . So the epoxidised compounds do not give a permanent
stabilisation.

Model epoxides such as epoxybutane undergo polymerisation in the presence of a strong Lewis
acid as ZnCl$_2$ through the opening of the oxirane ring. Thus the zinc atom is incorporated at
the end of the polyether chain but the Zn - O bond is sensitive to HCl. Otherwise using cou-
lometric titration of the chlorides in the polymer matrix, epoxidised soya bean oil has been
found to delay the appearance of ZnCl$_2$. The induction period as well as the rate formation
of metal chloride is proportional to the initial concentration of oxirane ring in the reci-
pe (Ref. 13).

Although it has been shown that epoxidised compounds are partly grafted onto the polymer du-
ring the processing operations their ability to react with metal chlorides which are strong
Lewis acid as ZnCl$_2$ or CdCl$_2$ is the true explanation of their synergistic action.

Nevertheless it is to be noted that stearic acid parallels chlorides formation (Ref. 8) and finally the ternary system Zn - Ca - epoxidised soya bean oil acts as HCl acceptor.

α-phenylindole (Ref. 15 & 8). During processing at 180°C α-phenylindole retards initial discoloration and a pink colour appears at about 25 % chloride yield, the blackening being observed later at about the same chloride yields as for the basic recipe (50 %).

The pink colour is the same as was previously observed during interaction of α-phenylindole with chlorohexene or HCl in dichloroethane and due to a hydrogen chloride - α-phenylindole complex (Ref. 15). For this reason the α-phenylindole must be used in presence of HCl acceptors.

From model compound studies it has been shown that α-phenylindole reacts with allylic chlorine atoms through a C-alkylation according to the reaction (6) (Ref. 15) where
R = CH_3 - CH = CH - CH - CH_2 - CH_3 :

(6)

(I)

A disubstituted product (II) has been identified and in the presence of $ZnCl_2$ a trisubstitution reaction may take place (III) :

(II)   (III)

The HCl does not react with the products of C-alkylation and for that reason the stabilisation through a such reaction is permanent.

During the processing at 180°C on a rolling mill a large amount of α - phenylindole is grafted onto the polymer as shown by GPC (Ref. 8). This grafting reaction tends to decrease the mean lenght of conjugated polyene sequences so that the initial yellow colour is prevented.

Nevertheless as α-phenylindole does not delay very much the accumulation of chlorides in the polymer matrix and as it does not retard the sudden blackening of the polymer it can be classified as a short-term secondary stabiliser especially useful to prevent initial discoloration.

β-diketone compounds (Ref. 9). A recent patent claims the steraoyl-benzoyl methane as a co-stabiliser to improve the efficiency of the stabilisation recipes based upon the combination of the zinc-calcium soaps. The benzoylacetone is a model compound of this stabiliser.

The favorable effect of the benzoylacetone on the initial discoloration is linked to the definitive substitution reaction of the allylic chlorine atoms through a C-alkylation that contributes to shorten conjugated polyene sequences. The C-alkylation takes place only in the presence of $ZnCl_2$ as catalyst according to the reaction (7) where R = CH_3 - CH = CH - CH - CH_2 - CH_3 and in the recipes with zinc soaps as shown Fig. 3 where the response of the UV detector is sensitive to the benzoylacetone grafted onto the polymer after processing on a rolling-mill at 180°C :

(7)

This reaction changes drastically the percentage of the enol rate and causes in the infrared spectrum the appearance of two bands at 1720 cm^{-1} and 1680 cm^{-1} assigned respectively to the CH_3 - C - and C - groups. These two bands can be used to follow the progress of the grafting of the benzoylacetone onto the polymer.

Otherwise the benzoylacetone tends to accelerate the dehydrochlorination of the PVC and also the accumulation of metal chlorides when the molar Ca/Zn ratio has values from 0.5 to 2. This finding contributes to shorten the sudden blackening time and it is a short-term stabiliser.
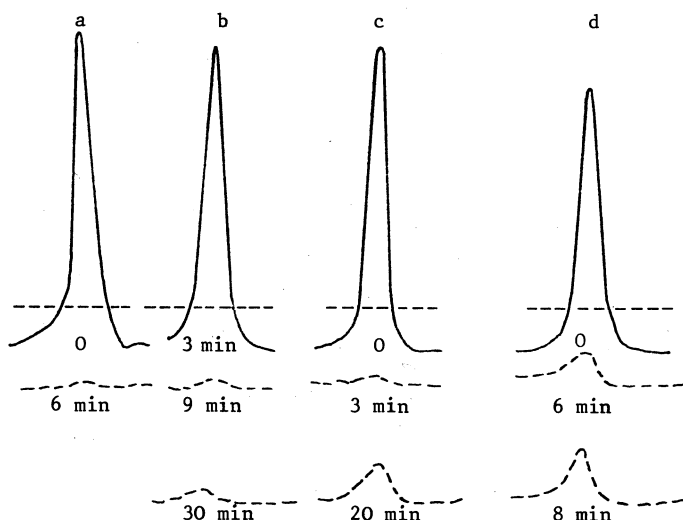
Fig. 3. GPC chromatograms - (-----) UV detection ; (———) refractometric detection

a) PVC 100 phr   ; b) PVC 100 phr
   benzoylacetone 0.86 phr   calcium stearate 3.2 phr
                                           benzoylacetone 0.86 phr

c) PVC 100 phr   ; d) PVC 100 phr
   calcium stearate 2.13 phr   calcium stearate 1.06 phr
   zinc stearate 1.1 phr   zinc stearate 2.23 phr
   benzoylacetone 0.86 phr   benzoylacetone 0.86 phr

Polyols. Sorbitol strongly retards the accumulation of metal chloride in a similar way to epoxy compounds. The polyols are not stable under the conditions of PVC processing and their role remains to be elucidated probably through the identification of their decomposition products.

Phosphites. From our studies with chlorohexene (Ref. 5) only alkyl phosphites are able to react with allylic chlorine atoms according to the Michaelis. Arbuzov reaction (8) where $R = CH_3 - CH = CH - CH - CH_2 - CH_3$:

$$RCl + P(OR')_3 \longrightarrow R' - O - \overset{O}{\underset{R}{\overset{\|}{P}}} - O - R' + R'Cl \tag{8}$$
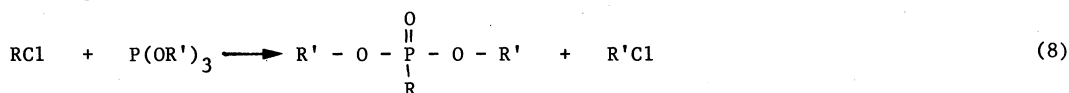
$ZnCl_2$ is a catalyst for this reaction but the rate constants of the elimination and substitution are close together.

The phosphonate ester is sensitive to HCl and may be decomposed with regeneration of allylic chlorine atoms.

Phosphites react also with HCl according to the reaction (9) :

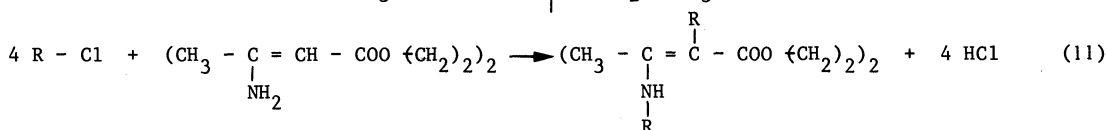$$P(OR)_3 + HCl \longrightarrow RCl + 2(RO)P\overset{\nearrow O}{\underset{\searrow H}{}} \tag{9}$$
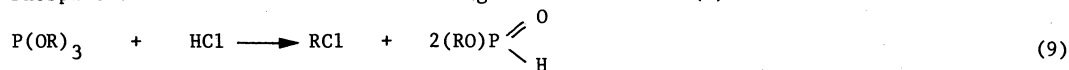
Otherwise the introduction of either alkyl or aryl phosphites in the combination of Zn-Ca soaps does not change the rate of the chloride accumulation. This finding shows that the reaction of the phosphites with $ZnCl_2$ according to the reaction (10) suggested by Briggs and Wood (Ref. 16) as an explanation of the synergistic action of such compound does not appear to occur to a large extent   in the polymer matrix.

$$ZnCl_2 + 2 P(OR)_3 \longrightarrow 2 (RO) \overset{O}{\overset{\|}{P}} - Zn - \overset{O}{\overset{\|}{P}} (OR)_2 + 2 RCl \tag{10}$$
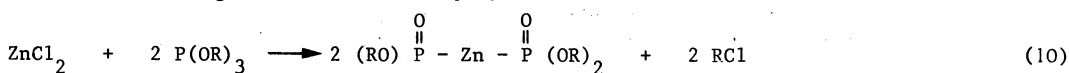
An other explanation must be given for the synergistic action of the phosphites. Such compounds are well-known to be peroxide decomposers and this role may be the most important in the processing operations.

β-aminocrotonate esters (Ref. 17 & 13). Our studies with chlorohexene (Ref. 17) give indication that N-alkylation takes place first and is followed by a C-alkylation according to the reaction (11) ; where $R = CH_3 - CH = CH - CH - CH_2 - CH_3$:

$$4 \ R - Cl \ + \ (CH_3 - \underset{\underset{NH_2}{|}}{C} = CH - COO \ (CH_2)_2)_2 \longrightarrow (CH_3 - \underset{\underset{\underset{R}{|}}{N\!H}}{C} = \overset{\overset{\overset{R}{|}}{}}{C} - COO \ (CH_2)_2)_2 \ + \ 4 \ HCl \qquad (11)$$

In the polymer matrix butanediol β-aminocrotonate is proved to strongly delay the chlorides accumulation more than epoxidised soya bean oil (Ref. 13). Thus it is also a long term stabiliser. Unfortunately in the PVC matrix secondary reactions liberates ammonia probably through the action of HCl.

Conclusion. In conclusion progress has been made towards a knowledge of the exact role played by the various components of a stabilising recipe.

The basic chemistry of the substitution reaction through O-alkylation by metal soaps or epoxy compounds, P-alkylation by phosphites, C-alkylation by α-phenylindole and its derivatives or by β-diketone or by aminocrotonate esters and also N-alkylation by these last compounds is now well established.

The catalytic action of zinc chloride in HCl elimination and in the substitution of the previous organic groups has been demonstrated.

The different functions of the short-term and long term secondary stabilisers have been elucidated. Short-term stabilisers react through C- or N- alkylation and then lead to HCl and $ZnCl_2$ formation. In this way they improve the efficiency of the catalysis of the substitution of the allylic chlorine atoms located at the end of a growing polyene chain. The polyene sequences are thus shortened so that coloration is delayed. On the other hand they cause an increase of the concentration of metal chlorides and may then lead finally to an enhanced rate of degradation and a sudden blackening and crosslinking of the polymer. For this reason they have to be used in conjunction with a long-term stabiliser which will prevent the accumulation of $ZnCl_2$ and will moderate its catalytic action as well in substitution reaction as in dehydrochlorination reaction.

The secondary stabilisers must be carefully selected to obtain the best compromise between final coloration of the polymer after processing and sudden blackening during the processing.

THE MECHANISM OF ACTION OF ORGANOTIN STABILISERS

Our previous studies have shown that metal chlorides ($ZnCl_2$ or $CdCl_2$) as Lewis acid play a central role in the substitution reaction of allylic chlorine atom and HCl elimination through the formation of the intermediate allylic carbocation. These two reactions are always competitive and the accumulation of metal chlorides which are strong Lewis acid causes the blackening and crosslinking of the polymer.

We have studied the catalytic action of the different chloroalkyltin as by-products of tin stabilisers with respect to the dehydrochlorination using the chlorohexene and the PVC itself. In this case the thermal degradation is carried out in sealed glass ampoules containing the polymer and the tin compound. After sealing, the glass ampoule is put in a oven at 180°C and then is broken inside a mixture of tetrahydrofuran and methanol (20 % in volume) in the presence of CaO which will react with HCl to give $CaCl_2$ titrated by coulometry.

From our studies only butyl tin trichloride is able to cause the elimination reaction and also the oligomerisation of the hexadiene. It is interesting to note that the catalytic activity of the butyl tin trichloride is similar to that of $ZnCl_2$. Tributyl tin chloride is not able to initiate the dehydrochlorination of the chlorohexene. This last reaction is very slow in presence of dibutyl tin dichloride (10 % yield after four hours in the dichloroethane as solvent). Most of the stabilisation recipes using organotin stabilisers involve dialkyl tin compound which ultimately lead to dialkyl tin dichloride. A such compound is not a very bad catalyst for the degradation. For that reason catastrophic blackening are not observed with tin stabilisers as it is for the combination of Zn - Ca soaps because of the catalytic activity of zinc chloride with respect to the dehydrochlorination.

If the number of chlorine atoms plays the main role in the strength of the Lewis acidity of the alkyl tin derivatives the nature of the alkyl group has also an influence as shown in the next table I where are summarized the rate constant of HCl elimination (K) obtained from the chlorohexene degradation and the Mossbauer data giving the isomer shift for various dialkyl tin dichlorides $(R)_2SnCl_2$.

TABLE 1. Kinetic and Mössbauer data (Ref. 19) of various dialkyl tin dichlorides in the degradation of the chlorohexene

$(R)_2 SnCl_2$	$K.10^5$ $(mole^{-1}.1^{-1}.s)$	Isomer shift $(mm.s^{-1})$
$(n.octyl)_2 SnCl_2$	12	1.731
$(n.butyl)_2 SnCl_2$	18	1.624
$(methyl)_2 SnCl_2$	30	1.551
$(phenyl)_2 SnCl_2$	42	1.387

The isomer shift is proportional to the electron density of the tin atom which is affected by electron donating power of the alkyl group bonded to the tin atom. In consequence the isomer shift varies in a opposite way with the strength of the Lewis acidity.

Thus di-n-octyl tin dichloride has the weakest Lewis acidity and the di-phenyl tin dichloride has the strongest Lewis acidity. We have found a direct correlation between the strength of the Lewis acidity of the dialkyltin dichlorides and their influence both on the HCl elimination from the chlorohexene and from the PVC (Fig. 4).
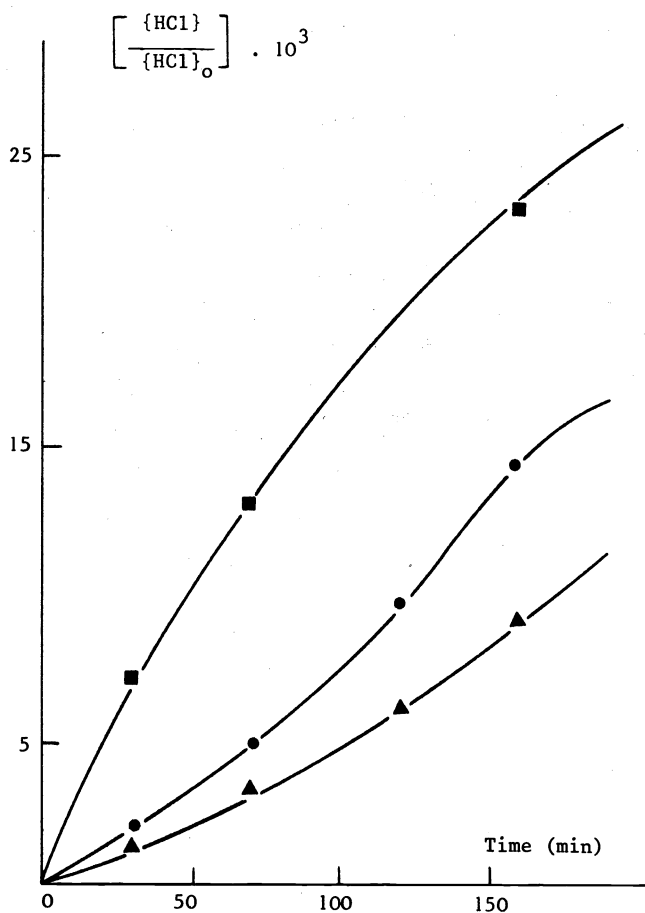
Fig. 4. PVC degradation at 180°C (200 g) in presence of 13.10^{-6} mole of $(phenyl)_2 SnCl_2$ (■) ; $(n-octyl)_2 SnCl_2$ (▲) ; $(n-butyl)_2 SnCl_2$ (●)

Using ^{1}H-NMR spectroscopy, we have shown (Ref. 20) also that dialkyl tin dithioglycolate esters can substitute allylic chlorine atoms through an ionic mechanism in which the rate determining step is yet the formation of the allylic carbocation. When dialkyl tin monochloride thioglycolate ester replaces dialkyl tin dithioglycolate esters the reaction begins at

lower temperature and is more rapid.

Furthermore we have shown also that free thioglycolate reacts with chlorohexene and this reaction is also more rapid than that of the alkyl tin derivatives. This conclusion suggests an indirect route for the substitution reaction. HCl produced by a small amount of elimination from the allylic carbocation might be enough to start the process because it reacts immediately with tin thioglycolate to give thiol which would react with chlorohexene with regeneration of HCl.

GENERAL CONCLUSION

In general conclusion the previous review shows that the metal soaps, tin stabilisers and organic compounds as secondary stabilisers function in the PVC stabilisation through an ionic mechanism. The rate determining step is the formation of allylic carbocation which is favoured by the presence of metal chlorides with a strong Lewis acidity as $ZnCl_2$, $CdCl_2$ or $RSnCl_3$. The reactions of stabilisation keep allylic structures in PVC backbone after reaction with the stabilisers and most of them are not stable towards HCl so that the stabilisation process is not permanent. Otherwise such unsaturated structures formed during the processing are able to promote photo-oxidation process. Thus to progress in the PVC stabilisation from thermal or photochemical point of view it would be necessary to promote a new class of stabilisers leading to the elimination of the polyene structures.

REFERENCES

1. L.F. Smith, H.E. Ungnade, W.M. Lauer and R.M. Leerley, J. Amer. Chem. Soc. 61, 3079 (1939)
2. R.S. Airs, M.P. BALFE and J. Kenyon, J. Chem. Soc. 18 (1942)
3. A. Michel, A. Guyot and D. Nölle, Polymer degradation and stability – Applied Science Publishers (to be published)
4. Tran Van Hoang, A. Michel, C. Pichot and A. Guyot, Europ. Polym. J. Vol. 11, pp. 469-474 (1975)
5. Tran Van Hoang, A. Michel and A. Guyot, Europ. Polym. J. Vol. 11, pp. 475-482 (1975)
6. Tran Van Hoang, A. Michel and A. Guyot, Europ. Polym. J. Vol. 12, pp. 337-346 (1976)
7. Tran Van Hoang, A. Michel, A. Revillon, M. Bert, A. Douillard and A. Guyot, Meeting ACS, New Orleans – Advances in Chemistry series 169, p. 374 (1978)
8. Tran Van Hoang, A. Michel and A. Guyot, J. of Polym. Degrad. and Stab. 1, 237 (1979)
9. A. Michel, Tran Van Hoang, B. Perrin and M.F. Llauro, J. Polym. Degrad. and Stab. (to be published)
10. M. Onozuka and M. Asahina, Rev. in Macromol. Chem. 4, p. 235 (1970)
11. D.F. Anderson and D.A. McKenzie, J. Polym. Sci. Part A1, p. 2905 , 8(1970)
12. E. Czako, Z. Vymazal, Z. Volka, I. Stibor and J. Stepek, Europ. Polym. J. 15, p. 81 (1979)
13. A. Michel, Tran Van Hoang et A. Guyot, Meeting ACS, New Orleans – Advances in Chemistry series 169, p. 386 (1978)
14. Tran Van Hoang, A. Michel and A. Guyot, Europ. Polym. J. Vol. 12, pp. 347-356 (1976)
15. Tran Van Hoang, A. Michel and A. Guyot, Europ. Polym. J. Vol. 12, PP. 357-364 (1976)
16. G. Briggs and N.E. Wood, J. Appl. Polym. Sci. 15, p. 25 (1971)
17. Tran Van Hoang, A. Michel and A. Guyot, J. of Macromol. Sci., Chem A12(3), pp. 411-440 (1978)
18. Tran Van Hoang, A. Michel and A. Guyot, J. of Polym. Degrad. and Stab. (to be published)
19. Mössbauer Effect Data Index edited by J.G. Stevens and V.E. Stevens
20. A. Michel, A. Guyot and D. Nölle, J. of Degrad. and Stab. (to be published)