JOURNAL OF MATERIALS SCIENCE 20 (1985) 3816–3830

Review

True stabilization: the behaviour of lead compounds against the thermal decomposition of polyvinyl chloride

E. W. J. MICHELL
Cookson Group plc, Central Research Laboratories, 7 and 11 Wadsworth Road, Perivale, Greenford, Middlesex, UK

Investigations which have been conducted within the last two decades into the behaviour of basic lead compounds as stabilizers against the thermal dehydrochlorination of polyvinyl chloride are summarized. It is shown that the results can be explained satisfactorily in terms of a free radical dehydrochlorination mechanism and a regenerative exchange process which interferes with the dehydrochlorination. This may be regarded as "true stabilization" in contrast to "hydrogen chloride scavenging". In true stabilization it is proposed that aliphatic carboxylate groups (such as the stearate ion) react with reservoirs of basic lead compounds (such as white lead) to form relatively mobile salts (such as stearates of lead). Also, it is proposed that these salts take part in exchange reactions with chlorine atoms released by the PVC during free radical decomposition, to give innocuous chlorides of lead and the corresponding aliphatic carboxylate free radicals. Hence the chlorine atoms are trapped and no longer able to propagate dehydrochlorination of the polymer. Further, it is proposed that the aliphatic carboxylate free radicals can esterify PVC chains at sites where prior attack by chlorine atoms has abstracted methylenic hydrogen atoms leaving unpaired electrons. This step eliminates the stimulus for loss of chlorine atoms from the PVC, thereby also interfering with the free radical propagation mechanism. Subsequently, the pendant aliphatic carboxylate groups dissociate from the polymer chains with neighbouring chloromethylenic hydrogen atoms to form the corresponding acids, and leaving the chlorine atoms adjacent to carbon–carbon double bonds in relatively stable vinyl-type positions. The aliphatic carboxylic acids so formed can react with the basic lead compounds reservoir to regenerate mobile salts so that the stabilizing process is therefore continuous and cyclic. It is demonstrated that ionic and unimolecular mechanisms which normally are put forward to explain the behaviour of primary stabilizers in PVC are not satisfactory because they do not account for all observations made with basic lead stabilizing regimes. Other evidence which favours the free radical decomposition and stabilization mechanisms is cited, and a suggestion is made for further work.

0022–2461/85 $03.00 + .12

1. Introduction

Polyvinyl chloride (PVC) is one of the more widely used synthetic polymers. Recent market surveys [1, 2] indicate that several million tons, representing about 20% of the total for all synthetic polymers, are consumed annually throughout the world. One reason for this popularity is the relatively low cost of manufacture from acetylene or from petrochemicals. Another reason is that the properties of PVC can be modified by additives to suit many purposes [3].

Unfortunately, PVC degrades at the temperatures required for softening (which are those most useful for processing) to give highly coloured solids with generally inferior properties, and yielding large quantities of hydrogen chloride (HCl) [4]. In practice, these undesirable effects of degradation are alleviated by "stabilizers". The stabilization technique evolved from the facts that early vinyl ester polymers contained free acids remaining from the monomer preparations, and that attempts were made to improve the polymers by neutralizing these acids with inorganic bases or with organic bases [5].

In retrospect it seems a short step to the deliberate additions some fifty years ago [6] of lead compounds (including white lead, lead monoxide and the salts of organic acids, such as lead butyrate), and various salts of other metals, to stabilize PVC whilst hot processing. By no means all of these additives were successful, and many were discarded as being useless or even detrimental to PVC for one reason or another. However, a few trials succeeded, and it is interesting to note that white lead (basic lead carbonate) and lead monoxide were used as stabilizers for the manufacture of plasticized PVC cable sheathing in 1944 [7]. White lead is still used for this purpose, and other basic lead salts (such as the two basic lead sulphates, $3PbO_2 \cdot PbSO_4 \cdot H_2O$ and $4PbO \cdot PbSO_4 \cdot 0.25H_2O$) are widely used for stabilizing plasticized and rigid PVC.

For the well-being of process machinery and of machine operators, an obvious function of all stabilizers is to prevent the release of HCl from hot PVC. Since lead stabilizers are basic salts it is not surprising that they might be regarded as scavengers for HCl. Thus, they would be expected to take part in simple acid base reactions such as that depicted by Equation 1, in which A represents a divalent anion:

$$n\mathrm{PbO \cdot PbA} + 2n\mathrm{HCl} \rightarrow n\mathrm{PbCl_2} + \mathrm{PbA} + n\mathrm{H_2O} \qquad (1)$$

Indeed, authoritative texts concerned with PVC stabilizers quote "safe lead contents" based on this reaction stoichiometry [8–10]. However, there are reasons to believe that HCl scavenging is not the only function of basic lead stabilizers.

First, a glance at lists of effective stabilizers for PVC [4, 8–10] shows that basic salts of metals other than lead are not used for this purpose. Thus, the metal soaps have formulae such as that indicated by $M(RCOO)_2$, and the tin stabilizers have formulae such as that indicated by R_2SnY_2, and all are neutral salts. These lists therefore exclude many inorganic bases which could scavenge HCl. It follows that basic lead compounds have properties which are favourable to PVC. Indeed, if this was not so, then white lead would not be among the few good stabilizers to have been used in PVC processing for the last fifty years.

Second, the above comment that lead stabilizers have favourable characteristics is justified by the practical observations that desirable properties of PVC are largely preserved when basic lead compounds are used in hot processing, whereas these properties deteriorate markedly in the absence of stabilizers. Thus, undesirable colour development is restricted when PVC is stabilized by white lead [4]. Also mechanical strength is retained in PVC stabilized with basic lead compounds. Furthermore, good electrical properties are retained in flexible PVC processed with basic lead stabilizers. (In fact, dibasic lead phthalate is found to be the best of all stabilizers in cable sheathing which is to be used at high temperatures for extended periods, such as in electric blankets [8–10]).

Features of this kind have prompted investigations in these laboratories designed to find out how basic lead compounds stabilize PVC. It is the aim of this paper to review work published during the last fifteen years or so which has directed the present author to a free radical stabilizing mechanism. This explains how lead compounds retard thermal dehydrochlorination in PVC and may be designated "true stabilization" in distinction from HCl scavenging.

2. Experimental details

PVC sheets have been prepared with thicknesses between 1.0 and 1.5 mm to various formulations on laboratory two roll differential mills using standard procedures. Portions of these sheets have been used for Congo-red tests at 180° C, either in air according to the normal proceedure, [11, 12] or in flowing nitrogen, to ascertain periods of efficient stabilization.

Portions of some sheets were heated in air at 180° C and then examined by optical microscopy (OM) and X-ray powder diffraction (XRPD) to study disperse crystalline lead salts. For these examinations the heated samples were mounted in paraffin wax and sectioned across their lengths using a biological microtome. Then the sections were mounted in parallel arrays for study in transmission (so that the results were typical of the whole samples) [13, 14]. The OM work was performed with polarized and unpolarized light using linear magnifications up to about 1250 times. The XRPD work was performed with monchromatic Cu$K\alpha$ X-radiation using a Nonius Guinier-de Wolff quadruple focusing camera.

Portions of other sheets were heated in flowing nitrogen, and carbon dioxide (CO_2) evolved from basic lead carbonate stabilizers was measured. The heated samples were examined by XRPD in transmission using the Guinier-de Wolff camera, [15] or in reflection using a Siemens (model F) X-ray powder diffractometer, in both cases with X-radiation from copper targets. The diffractometer examinations of microtomed sections again represented the bulk materials [16]. However, diffractometer studies of relatively large flat samples gave results which were typical of shallow surface layers [17].

Supplementary experiments on reactions without any PVC were also performed.

3. Results

3.1. Preliminary experiments

3.1.1. White lead stabilizer in a plasticized PVC sheet with stearic acid lubricant [13]

A PVC sheet was milled with fifty parts by weight per hundred parts of resin (50 phr) dialphonyl phthalate (DAP) plasticizer using 5 phr white lead (mainly hydrocerussite $2PbCO_3 \cdot Pb(OH)_2$, in this case) and 0.5 phr commercial stearic acid. OM showed that the tabular white lead crystals were oriented more or less parallel to the sheet surfaces, and XRPD did not detect any crystalline phases other than the stabilizer.

On heating samples in air, OM showed that a new particulate phase crystallized away from the white lead, but XRPD could not identify it. For ease of reference it has been called "basic lead chloride X" (BLCX) [18]. On further heating, this BLCX started to react and neutral lead chloride ($PbCl_2$) was found to crystallize away from the white lead and BLCX particles. Eventually the white lead and BLCX reacted completely and only $PbCl_2$ could be recognized. At this stage HCl was evolved from hot samples during Congo-red tests in air.

3.1.2. Effects of plasticizer and lubricant [19]

Parallel series of sheets were milled with various dioctyl phthalate (DOP), $C_6H_4(COOC_8H_{17})_2$, platicizer contents from zero (rigid PVC) to 100 phr. Either hydrocerussite or tribasic lead sulphate, $3PbO \cdot PbSO_4 \cdot H_2O$, was used as stabilizer at 5 phr, and each sheet was milled with either commercial stearic acid or with polyethylene lubricant at 0.5 phr. Congo-red tests were performed in air at 180° C, and various samples heated to these stages were examined by OM and by XRPD.

It was found that the sheets milled with stearic acid were generally better stabilized than those milled with polyethylene. OM showed that $PbCl_2$ was formed as relatively large crystals (10 μm long) at the Congo-red test-times in sheets milled with 15 to 50 phr plasticizer and with stearic acid lubricant. Also, BLCX could be recognized in these samples. However, in the absence of DOP or of stearic acid these product phases were observed as submicron particles. In the absence of both DOP and stearic acid, no product phases could be observed by OM, but XRPD showed that substantial amounts of $PbCl_2$ were formed. Unreacted stabilizer was found in nearly all of the samples heated to the Congo-red test-times and small proportions ("very minor" and "trace") of anhydrous neutral lead orthophthalate (ANLOP), $PbC_6H_4(COO)_2$, were found in some samples by XRPD.

3.2. Evolved CO_2 and XRPD studies

3.2.1. *Plumbonacrite as the stabilizer in plasticized and in rigid PVC both with stearic acid lubricant [15]*

Plumbonacrite, $6PbCO_3 \cdot 3Pb(OH)_2 \cdot PbO$ [20] differs somewhat in chemical stoichiometry from hydrocerussite. Both of these hydrated basic lead carbonates occur in commercial white lead stabilizers, and pure samples of each can be made for laboratory experiments.

Two PVC sheets were milled with 10 phr plumbonacrite and 0.5 phr commercial stearic acid. One sheet was rigid and the other was plasticized with 50 phr DOP. Portions of each were heated at 180° C under nitrogen for various periods up to the respective Congo-red test-times (36.5 h for the plasticized PVC and 11.6 h for the rigid PVC), and evolved CO_2 was measured. Sections of each sample were examined by XRPD using the Guinier-de Wolff cameras as before.

It was found that CO_2 was evolved continuously according to first order kinetics, but at faster rates from the rigid than from the plasticized PVC during these experiments. XRPD showed that the plumbonacrite was converted into chlorides of lead. In the plasticized samples, BLCX was formed and reacted to give $PbCl_2$ as before (Section 3.1.1). In the rigid samples, tribasic lead chloride (TBLC), $3PbO \cdot PbCl_2 \cdot nH_2O$, and BLCX were formed in sequence, but $PbCl_2$ was not detected. Very small (trace) proportions of ANLOP were found in two plasticized samples heated for relatively short periods. For each PVC sheet, stabilization was efficient whilst the plumbonacrite lasted and failed soon after this stabilizer had all reacted. Substantial proportions of BLCX remained at the Congo-red test-times (minor in the plasticized and major in the rigid material).

3.2.2. *Hydrocerussite stabilizer in plasticized PVC with stearic acid lubricant: bulk studies [16]*

A PVC sheet was milled with 50 phr DOP, 10 phr hydrocerussite and 0.5 phr commercial stearic acid. Portions were heated at 180° C under nitrogen for various periods up to the Congo-red test-time (about 43 h) and evolved CO_2 was measured. Sections were cut for examination by XRPD using the Siemens X-ray powder diffractometer.

It was found that CO_2 was evolved continuously according to first order kinetics from these samples (but at rates different from those observed for plumbonacrite; Section 3.2.1). Quantitative XRPD measurements confirmed the rate constant and half-life for hydrocerussite reaction, and qualitative XRPD showed that this stabilizer was converted into BLCX which reacted to form $PbCl_2$. Also, small amounts of ANLOP were detected in some samples heated for relatively short periods. However, in contrast to the work with plumbonacrite (Section 3.2.1) it was found that stabilization continued long after the hydrocerussite had all reacted (at about 21 h heating) and long after the BLCX had been converted into $PbCl_2$ (at about 33 h heating).

3.2.3. *Hydrocerussite stabilizer in plasticized PVC with stearic acid lubricant: surface studies [17]*

Relatively large portions of heated samples from plasticized PVC containing hydrocerussite were examined on the Siemens X-ray powder diffractometer. In contrast to the above studies of thin sections representing the bulk samples (Section 3.2.2), these examinations represented shallow surface layers.

Quantitative XRPD showed that the hydrocerussite reacted continuously according to first order kinetics in these surface layers, and at rates virtually identical to those found for reaction in the bulk regions of these samples [16] (Section 3.2.2). Also, qualitative XRPD showed that the hydrocerussite was converted into BLCX and then $PbCl_2$ in these surface layers, both the hydrocerussite and the BLCX completely reacting long before stabilization failed at the Congo-red test-time. However, in contrast to the bulk regions, XRPD showed that lead salts of orthophthalic and stearic acids were formed in many of the surface layers. As well as salts of these individual acids, large proportions of a complex lead salt believed to contain both orthophthalate and stearate ions were observed. This complex salt was designated "unidentified phase C" (UPC) for convenience.

3.3. Supplementary experiments

3.3.1. *The reaction of HCl with white lead in hot DOP [21].*

Dry HCl was passed into a suspension of white lead (mainly hydrocerussite) in DOP at 182° C without any PVC. Samples were withdrawn at intervals and examined by XRPD using the Guinier-de Wolff camera. BLCX and ANLOP were both formed in concentrations which increased during the early stages of the experiment. Subsequently the BLCX reacted to form $PbCl_2$, but the ANLOP did not seem to be affected.

3.3.2. The reaction of plumbonacrite with hot DOP [22]

Pure plumbonacrite was reacted with DOP at 180° C under nitrogen. Anhydrous monobasic lead orthophthalate (AMBLOP), $PbO \cdot PbC_6H_4(COO)_2$, was the only crystalline reaction product in experiments of various durations.

3.3.3. The reaction of HCl with white lead in hot mineral oil [18]

Dry HCl was passed into a suspension of white lead (mainly hydrocerussite) in mineral oil (a liquid paraffin) at 177° C with no PVC or DOP. Samples were withdrawn at intervals and examined by XRPD using the Guinier-de Wolff camera. TBLC was formed as a fine particulate phase which reacted to give BLCX and $PbCl_2$ in sequence.

4. Discussion

4.1. Preliminary experiments

4.1.1. White lead stabilizer in a plasticized PVC sheet with stearic acid lubricant [13]

Three important features emerged from this work. First, it was evident that stabilizing reactions took place in solution. If this had not been so, the BLCX and $PbCl_2$ could not have grown as relatively large crystals at sites remote from each other and from the white lead stabilizer particles. Second, it was evident that the white lead reacted as an entity rather than as a mixture of lead oxide and lead carbonate. This refutes the idea of "safe lead content" for white lead, [8–10] which proposes that "the lead oxide part of basic lead carbonate reacts before CO_2 is evolved from reaction of the lead carbonate part". Third, for the first time, $PbCl_2$ was positively identified as the terminal product of basic lead stabilizer reactions. Previously this result had only been surmized.

4.1.2. Effects of plasticizer and lubricant [19]

Three important features emerged from this work. First, the results confirmed that efficient stabilization took place in solution. It was evident that the DOP plasticizer behaved as a solvent, and that the stearic acid lubricant had an important influence here (presumably by reacting with the basic lead stabilizer to give stearates of lead as the active soluble intermediates). Second, orthophthalates of lead were involved in stabilization to some extent. Third, unreacted stabilizers found by XRPD show that stabilization for samples heated in air is not always efficient.

4.2. Evolved CO_2 and XRPD studies

4.2.1. Plumbonacrite as the stabilizer in plasticized PVC and in rigid PVC both with stearic acid lubricant [15]

Three important features emerged from this work.

First, the fact that CO_2 was evolved continuously from these samples confirms the point made in Section 4.1.1, that basic lead carbonate stabilizers react as compounds, not as mixtures of lead oxide with lead carbonate. This completely refutes the idea of "safe lead content" as applied to white lead, [8–10] which originates from the fact that porosity (blistering) may occur if the processing temperatures are high (above 180° C). The correct reason here is that both PVC thermal dehydrochlorination and the associated stabilizing reactions, and thermal decomposition of the basic lead carbonate itself, accelerate with increasing temperature giving CO_2 which cannot all diffuse to escape from the hot material. Normally the CO_2 can diffuse to escape at temperatures below 180° C, and then cable sheathing can be extruded satisfactorily with white lead stabilizer.

Second, the fact that the CO_2 was evolved according to first order kinetics shows that the plumbonacrite stabilizer reacted at rates proportional to its own diminishing concentrations in the hot materials. This in turn shows that the PVC decomposition was being retarded. Thus, as chlorides of lead were formed, the overall concentrations of basic lead available for stabilization diminished. Hence, if the PVC had decomposed at some uniform (zero order kinetic) rate, either this would have out-paced stabilization (so that HCl would have been detected in the Congo-red test before the plumbonacrite had completely reacted), or the plumbonacrite would have reacted at rates faster than can be described by first order kinetics (in order to keep pace with decomposition of the PVC). However, neither of these alternatives was the case.

Third, the results for this plasticized PVC agree with those discussed in Sections 4.1.1 and 4.1.2 above. Thus, BLCX and $PbCl_2$ were formed in sequence (and some ANLOP was detected) suggesting that effective stabilizing reactions involved stearates of lead and took place in solution as before. However, TBLC was formed in the rigid PVC suggesting that there could have been direct reaction between the plumbonacrite stabilizer and HCl formed from the PVC ("HCl scavenging") in addition to the more efficient stabilizing reactions with stearates of lead.

On the basis of these findings a theory was proposed to explain how lead stabilizers retard PVC thermal decomposition ("true stabilization") [15] which will be discussed in Section 4.5.

4.2.2. *Hydrocerussite stabilizer in plasticized PVC with stearic acid lubricant: bulk studies [16]*

Three important features emerged from this work.

First, the general trends of CO_2 measurements and XRPD results agreed with the previous findings discussed in Sections 4.1.1 to 4.2.1 for plasticized PVC sheets milled with basic lead stabilizers and stearic acid lubricant, confirming the trends already observed.

Second, the fact that efficient stabilization continued long after the hydrocerussite had all reacted shows that the stabilizing regime retarded the PVC decomposition to almost negligible rates, and that it inhibited the formation of HCl. This was explained in terms of "true stabilization" as will be shown in Section 4.5.

Third, it was evident that less than the theoretically available quantity of CO_2 was evolved from experimentally heated samples when all of the hydrocerussite had reacted. This was due to reaction of stabilizer on milling the sheet with consequent loss of CO_2 prior to the experiments (again refuting the idea of "safe lead content" as applied to white lead).

4.2.3. *Hydrocerussite stabilizer in plasticized PVC with stearic acid lubricant: surface studied [17]*

Three important features emerged from this work.

First, agreement between the XRPD results for these surface examinations and those for the corresponding bulk studies (Section 4.2.2) shows that the hydrocerussite reacted more or less homogeneously throughout these hot samples, retarding the PVC decomposition to almost negligible rates (thereby preventing the formation of HCl, and so that efficient stabilization continued long after the hydrocerussite had all reacted).

Second, the accumulation of orthophthalates and stearates of lead in the surface regions of experimentally heated samples indicates that stearates of lead had migrated from the bulk to replace active intermediates already consumed in true stabilizing reactions. In turn this implies that orthophthalates of lead were largely responsible for true stabilization in the bulk (where carboxylates of lead did not crystallize).

Third, the fact that carboxylates of lead did not crystallize in the as-milled plasticized PVC sheet implies that all such compounds were used in true stabilizing reactions on the mill, combating PVC decomposition which was being promoted by oxidation. When the hot sheet was finally removed from the mill and set aside to cool only the surfaces would have been oxidized and stearates of lead could have migrated from the bulk to take part in true stabilization there (as suggested above). Subsequently, during the experimental heat treatments under nitrogen, relatively insoluble carboxylates of lead which were not used for true stabilization crystallized in these surfaces as mentioned above.

4.3. Supplementary experiments

4.3.1. *The reaction of HCl with white lead in hot DOP [21]*

The formation of ANLOP in large (major) proportions during this experiment without PVC contrasts with most of the results discussed above for plasticized PVC samples. This shows that HCl was seldom produced during the periods of efficient PVC stabilization in these experimentally heated materials, which supports the idea that true stabilization prevents the formation of HCl. Here it is interesting to note that, for heat treatments conducted in air (Section 4.1.2), true stabilization was not able to prevent the formation of HCl completely, and some ANLOP was formed by scavenging reactions in the PVC blends.

4.3.2. *The reaction of plumbonacrite with hot DOP [22]*

It can be expected that AMBLOP formed by this reaction could itself react with HCl to give ANLOP together with a chloride of lead (either basic or neutral depending on relative proportions) in the manner suggested by Equation 1 of Section 1. This would explain the results just discussed in Section 4.3.1. Again the general absence of ANLOP from plasticized PVC samples heated under nitrogen (Section 4.2.1 to 4.2.2) shows that HCl was hardly formed in them. Furthermore, the general absence of AMBLOP from these PVC samples shows that this compound was utilized in other stabilizing reactions. These features can be explained in terms of true stabilization as will be shown in Section 4.5. Here it is emphasized that the accumulation of carboxylates of lead in the surface regions of such materials can be explained in terms of true stabilization, as already mentioned in Section 4.2.3, rather than in terms of HCl scavenging.

4.3.3. *The reaction of HCl with white lead in hot mineral oil [18]*

The formation of TBLC which then reacted to give BLCX and $PbCl_2$ in sequence during this experiment resembles the sequence observed with plumbonacrite in rigid PVC (Section 4.2.1). This clearly suggests that HCl scavenging occurred in the rigid PVC, which contrasts with most of the results discussed above for plasticized samples. Nevertheless, as discussed in Section 4.2.1, other factors suggest that true stabilization retarded the PVC decomposition in these experimentally heated rigid samples.

4.4. PVC thermal dehydrochlorination

No discussion of stabilizing reactions in hot PVC is complete without considering thermal dehydrochlorination. Thus, it is important to realize that, whilst many behavioural features are well established, the actual mechanism of PVC thermal dehydrochlorination is a subject of controversy. It will be shown in Section 4.5 that only the free radical chain mechanism can be used to explain adequately the behaviour of lead stabilizing regimes.

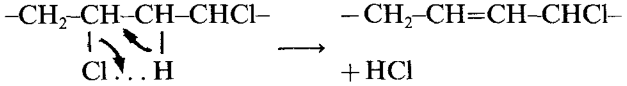
4.4.1. *Dehydrochlorination mechanisms*

Virgin PVC is intrinsically stable at room temperature, but it decomposes above 100° C to give highly coloured solids. Up to about 180° C HCl seems to be the only volatile, whilst between 180 and 300° C small amounts of benzene and some other hydrocarbons are evolved [23, 24]. Above 300° C increasing amounts of various hydrocarbons are formed and HCl becomes a minor volatile [25]. Dehydrochlorination of virgin PVC at moderate temperatures gives strong colours at low extents of reaction (when less than 0.1% of the theoretically available HCl has been lost) suggesting that polyene structures with seven or more conjugated double bonds are formed by a so-called "zipper" reaction [26]. This zipper reaction can be depicted as in Equation 2

$$\begin{array}{l}-(-\mathrm{CH_2}-\mathrm{CHCl}-)_n-(-\mathrm{CH}=\mathrm{CH}-)_m- \longrightarrow \\ -(-\mathrm{CH_2}-\mathrm{CHCl}-)_{n-1}-(-\mathrm{CH}=\mathrm{CH}-)_{m+1}- + \mathrm{HCl}\end{array} \qquad (2)$$

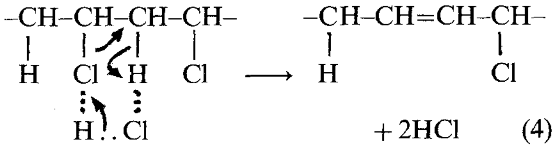
Three general schemes, which are known as "unimolecular dehydrochlorination", "ionic dehydrochlorination" and "free radical chain dehydrochlorination", respectively, have been proposed to explain the zipper process.

4.4.1.1. Unimolecular dehydrochloration [27]. It is suggested that a cyclic transition state in PVC can give unimolecular dehydrochlorination as depicted by Equation 3;



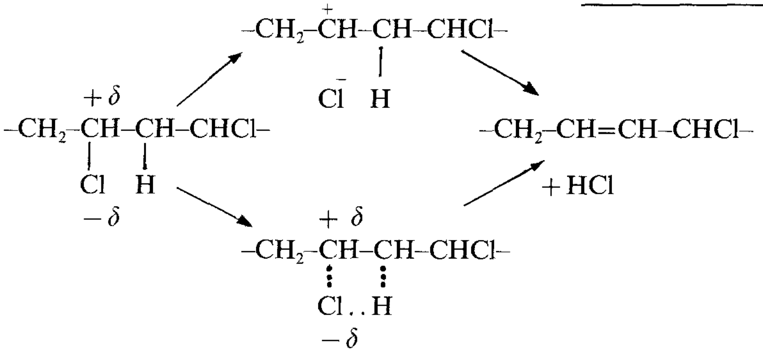
$$\underset{\mathrm{Cl}\cdots\mathrm{H}}{-\mathrm{CH_2}-\mathrm{CH}-\mathrm{CH}-\mathrm{CHCl}-} \longrightarrow \begin{array}{l}-\mathrm{CH_2}-\mathrm{CH}=\mathrm{CH}-\mathrm{CHCl}-\\ +\mathrm{HCl}\end{array} \qquad (3)$$

It is thought also that this process can be stimulated by carbon–carbon double bonds in allylic positions relative to the chlorine atoms (that is, in the backbone structural unit –CH=CH–CHCl–) so that zipper dehydrochlorination yields conjugated polyenes. Further, it is suggested that catalysis of the PVC dehydrochlorination by HCl can be explained in terms of a six-centred cyclic transition state as depicted by Equation 4:



(4)

4.4.1.2. Ionic dehydrochlorination. In this process it is thought that electronic charge separations connected with carbon–chlorine bonds (concealed ionization) will be accentuated by allylic unsaturation in PVC molecules, causing loss of chloride ions (Cl^-) and hydrogen ions (H^+) to give HCl molecules and new double bonds in the polymer chain [28]. The new double bonds formed by losses of the ions then activate further allylic charge separations, propagating the dehydrochlorination to give conjugated polyenes. This process can be depicted [29] as in Equation 5:



(5)

4.4.1.3. Free radical chain dehydrochlorination [30]. It is thought that a chlorine atom (which has an unpaired electron and therefore can be regarded as a free radical) attacks a PVC molecule, taking a methylenic hydrogen atom to give HCl and leaving an unpaired electron on the former methylenic carbon atom (an "active free radical site") in the PVC chain (which is therefore a macroradical) as depicted by Equation 6:

$$\dot{C}l + \text{-CH}_2\text{-CHCl-CH}_2\text{-CHCl-} \longrightarrow \text{-}\dot{C}\text{H-CHCl-CH}_2\text{-CHCl-} + \text{HCl} \qquad (6)$$

A chlorine atom then dissociates from an adjacent chloromethylenic group in the PVC chain, becoming a free radical and leaving a carbon–carbon double bond in the chain as depicted by Equation 7:

$$\text{-}\dot{C}\text{H-CHCl-CH}_2\text{-CHCl-} \longrightarrow \text{-CH=CH-CH}_2\text{-CHCl-} + \dot{C}l \qquad (7)$$

This chlorine atom can then attack the same PVC molecule, abstracting a methylenic hydrogen atom allylic to the double bond, thus forming HCl in the manner of Equation 6 and giving a new macroradical which can decompose according to Equation 7. The sequence of events is repeated, the chlorine atoms attacking methylenic groups adjacent to the carbon–carbon double bonds, so that a conjugated polyene system is developed, and a corresponding number of HCl molecules is formed. At some stage the chlorine atom released by one macroradical may attack another PVC molecule, thereby terminating dehydrochlorination in the first chain and initiating it in the second.

4.4.2. Dehydrochlorination kinetics

4.4.2.1. Dehydrochlorination under nitrogen or in vacuo. Theoretical analysis for the initiation, propagation and termination steps of a free radical chain mechanism in steady state conditions indicates first order kinetics for PVC thermal dehydrochlorination [31]. The proposed initiation steps were, first, cleavage of carbon–chlorine bonds to give chlorine atoms and macroradicals as in Equation 8:

$$\text{-CH}_2\text{-CHCl-CH}_2\text{-CHCl-} \longrightarrow \text{-CH}_2\text{-}\dot{C}\text{H-CH}_2\text{-CHCl-} + \dot{C}l \qquad (8)$$

and, second, reaction of the macroradicals with PVC molecules, abstracting methylenic hydrogen atoms and giving new macroradicals as in Equation 9:

$$\mathrm{-CH_2-\dot{C}H-CH_2-CHCl- + -CH_2-CHCl-CH_2-CHCl- \longrightarrow}$$

$$\mathrm{-CH_2-CH_2-CH_2-CHCl- + -\dot{C}H-CHCl-CH_2-CHCl-} \qquad (9)$$

It was suggested that propagation then follows the scheme of Equations 6 and 7 in Section 4.4.1.3 involving the chlorine atoms formed as in Equation 8 and the macroradicals formed as in Equation 9. The deduced first order kinetics agree with simultaneous measurements of spin (unpaired electron, or free radical) generation rates and of dehydrochlorination rates under nitrogen, for which the same authors found an initial slow phase followed by rapid first order degradation and then a limiting phase with no further reaction [32]. On the basis of the kinetic analysis, activation energies were deduced [31] which agree with measured values for dehydrochlorination of structurally different PVC samples.

For PVC samples of different molecular weights it has been found that thermal dehydrochlorination rates under nitrogen increase with the number of chain ends, that is with decreasing molecular weight [33–35]. It was suggested [33] that dehydrochlorination depends on the dissociation from chain-ends of polymerizing free radical initiator residues to give mobile residue free radicals and PVC macroradicals as in Equation 10:

$$\mathrm{R-CH_2-CHCl-CH_2-CHCl- \longrightarrow}$$

$$\mathrm{\dot{R} + \dot{C}H_2-CHCl-CH_2-CHCl-} \qquad (10)$$

and it was demonstrated that small additions of dibenzoyl peroxide (which can be used as a source of benzoyl-oxy free radicals in polymerizing vinyl chloride) actually stimulated PVC dehydrochlorination. It was proposed [35] that the free radical residues abstract methylenic hydrogen atoms from PVC molecules to give new macroradicals as in Equation 11:

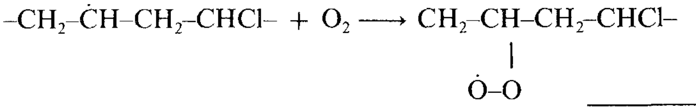
$$\mathrm{\dot{R} + -CH_2-CHCl-CH_2-CHCl- \longrightarrow}$$

$$\mathrm{RH + -\dot{C}H-CHCl-CH_2-CHCl-} \qquad (11)$$

The macroradicals formed as in Equations 10 and 11 would decompose by the chain process [30] (Equations 6 and 7 in Section 4.4.1.3). Further, it seems that PVC samples polymerized with different free radical initiators often differ in stability, that is they decompose at different rates [4, 25], indicating that some initiator residues dissociate from the chain ends more readily than others in free radical dehydrochlorination.

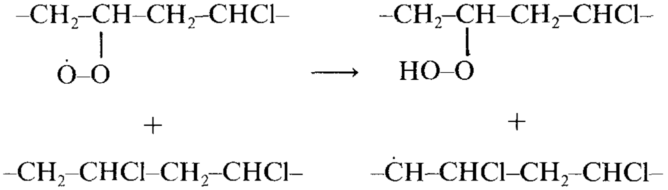
Various workers have found that isothermal PVC decomposition is essentially uniform (zero order kinetics) up to as much as 30% dehydrochlorination, proceeding at rates which differ with temperature between 150 and 250° C under nitrogen [34–36]. The initial slow phase followed by rapid first order dehydrochlorination [32] mentioned above could resemble zero order kinetics up to as much as 25% dehydrochlorination. A two thirds kinetic order deduced for PVC degradation between 235 and 260° C *in vacuo* [25] would simulate zero order kinetics up to about 17% dehydrochlorination, and these workers suggest a propagation mechanism identical to that described by Equations 6 and 7 in Section 4.4.1.3. Here it is useful to realize that the quantities of basic lead carbonate (10 phr) used in the CO_2 measurements and XRPD studies [15–17] discussed in Section 4.2 are equivalent to rather less than 5% dehydrochlorination. It could be expected that unstabilized PVC would decompose at approximately uniform rates (zero order kinetics) within this dehydrochlorination span when heated under nitrogen. This is a vital point in the reasoning that the lead stabilizing regimes actually retarded dehydrochlorination (Section 4.2.1).

4.4.2.2. Dehydrochlorination in air or oxygen. PVC thermal dehydrochlorination is faster in air or oxygen than under nitrogen [33–35, 37]. Simultaneous measurements of spin (unpaired electron or free radical) generation rates and of dehydrochlorination rates in oxygen [38] have been compared with measurements conducted under nitrogen (by the same authors [31]), and a mechanism was proposed to explain the higher rates in oxygen. It is thought that oxygen reacts with PVC macroradicals, formed by cleavage of carbon–chlorine bonds as in Equation 8, to give peroxide structures as depicted by Equation 12:



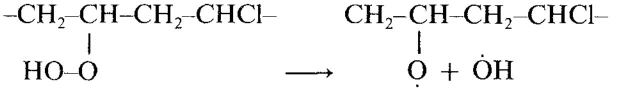
$$-CH_2-\dot{C}H-CH_2-CHCl- + O_2 \longrightarrow CH_2-\underset{\dot{O}-O}{\underset{|}{CH}}-CH_2-CHCl- \qquad (12)$$

These peroxy macroradicals then react with PVC molecules, abstracting methylenic hydrogen atoms to form unstable hydroperoxides and PVC macroradicals as in Equation 13:



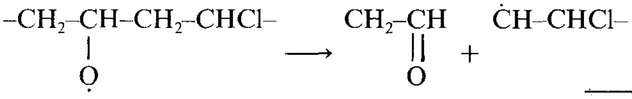
$$\begin{array}{ccc} -CH_2-\underset{\dot{O}-O}{\underset{|}{CH}}-CH_2-CHCl- & \longrightarrow & -CH_2-\underset{HO-\dot{O}}{\underset{|}{CH}}-CH_2-CHCl- \\ + & & + \\ -CH_2-CHCl-CH_2-CHCl- & & -\dot{C}H-CHCl-CH_2-CHCl- \end{array} \qquad (13)$$

The unpaired electrons in the PVC macroradicals stimulate chain dehydrochlorination as described in Section 4.4.1.3 and at this stage the same number of free radical centres as for dehydrochlorination under nitrogen is involved. However, the hydroperoxide structures can decompose giving oxy macroradicals and hydroxyl free radicals as depicted by Equation 14:



$$-CH_2-\underset{HO-O}{\underset{|}{CH}}-CH_2-CHCl- \longrightarrow CH_2-\underset{\underset{\cdot}{O}}{\underset{|}{CH}}-CH_2-CHCl- + \dot{O}H \qquad (14)$$

so that there are now more free radicals than during dehydrochlorination under nitrogen. Scission of the PVC backbone then may occur as depicted by Equation 15:



$$-CH_2-\underset{\underset{\cdot}{O}}{\underset{|}{CH}}-CH_2-CHCl- \longrightarrow CH_2-\underset{O}{\underset{||}{CH}} + \dot{C}H-CHCl- \qquad (15)$$

giving macroradicals which can decompose by the chain process described in Section 4.4.1.3. Hydroxyl free radicals may abstract methylenic hydrogen atoms from PVC molecules, giving water molecules and further macroradicals (which can decompose by the chain process) as depicted in Equation 16:

$$\dot{O}H + -CH_2-CHCl-CH_2-CHCl- \longrightarrow -\dot{C}H-CHCl-CH_2-CCl- + H_2O \qquad (16)$$

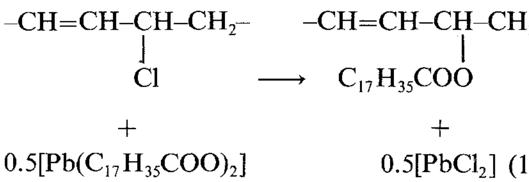
Hence it can be be seen that the number of free radical dehydrochlorination sites, and therefore the dehydrochlorination rates, in air or in oxygen increase to levels well above those for virgin PVC heated under nitrogen. This would explain why dehydrochlorination was potentially faster in the surfaces, requiring more efficient true stabilization than the bulk regions, of plasticized PVC samples experimentally heated under nitrogen after the surfaces had been oxidized in the last stages of milling, as described in Section 4.2.3.

4.5. Stabilizing mechanisms

4.5.1. A choice of mechanisms

It was mentioned in Section 1 that an important function of PVC stabilizers is to scavenge HCl whilst hot processing, and Equation 1 shows how basic lead salts could do this. However, it has been suggested by various authors [39–42] that stabilizers might also replace labile chlorine atoms allylic to carbon–carbon double bonds in the PVC, thereby inhibiting dehydrochlorination. Quoted in favour of this idea are the observations by infrared absorption spectroscopy [43] and by radioactive tracer methods [44] that carboxylate groups from barium, cadmium and zinc salts of 2-ethyl hexanoic acid become incorporated as ester groups in PVC molecules during stabilization, and by radioactive tracer methods [45] that the carboxylate groups from dialkyl tin carboxylates similarly become associated with the PVC.

This type of reaction for lead stabilizers has been written [42] as in Equation 17



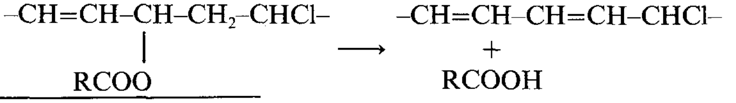
$$\begin{array}{ccc} -CH=CH-\underset{Cl}{\underset{|}{CH}}-CH_2- & \longrightarrow & -CH=CH-\underset{C_{17}H_{35}COO}{\underset{|}{CH}}-CH_2- \\ + & & + \\ 0.5[Pb(C_{17}H_{35}COO)_2] & & 0.5[PbCl_2] \end{array} \qquad (17)$$

and the justification for doing so was based on measurements of dehydrochlorination rates which show that lead stearate retards dehydrochlorination, whilst inorganic basic lead salts merely scavenge HCl, in static mixtures with PVC. Other workers [46] have found that lead stearate retards thermal dehydrochlorination of PVC dissolved in trichlorobenzene, or in bulk mixtures under dynamic conditions, and that tribasic lead sulphate with sufficient stearic acid to react with all the basic lead behaves in much the same way, whereas tribasic lead sulphate alone merely scavenges HCl. (It will be appreciated that these results [42, 46] accord with the work discussed in Section 4.1.2). However, as implied in Sections 4.2 and 4.3, and as will be shown in Sections 4.5.2 and 4.5.3, an alternative explanation to that depicted by Equation 17 is possible.

An underlying notion to the present author's research described in this paper is that any dehydrochlorination mechanism involving allylic unsaturation stimuli in the PVC molecules (such as the unimolecular and ionic processes outlined in Sections 4.4.1.1 and 4.4.1.2, respectively) could not be retarded continuously by lead stabilizing systems. Thus, unlike the metal soaps and the organo tin compounds, neutral lead salts are not used alone in PVC. In fact many lead stabilizing systems comprise a basic inorganic lead salt (such as white lead or a basic lead sulphate) together with a source of aliphatic carboxylate ions (such as stearic acid or a stearate of lead) in the lubricating system which is equivalent to perhaps one twentieth of the total lead content. The reasoning is then as follows.

First, if carboxylate ions in the lead stabilizing regime were to replace labile chlorine atoms as depicted by Equation 17, and if the resulting ester groups were so stable that they did not decompose releasing the carboxylate groups together with hydrogen atoms from adjacent methylenic groups to form the acid molecules, there could be no regeneration of lead carboxylates. Then, after all the lead carboxylate in the stabilizer/lubricant system had reacted, the remaining inorganic basic lead stabilizer would only scavenge HCl. (This argument is supported by the independent research [42, 46] mentioned already.) Hence, it could not be expected that PVC thermal dehydrochlorination would be continuously retarded, which conflicts with the findings discussed in Sections 4.2 and 4.3. Furthermore, it could not be expected that carboxylates of lead would crystallize in plasticized PVC samples after heat treatment, which conflicts with the XRPD studies of surface regions discussed in Secton 4.2.3.

Second, if the aliphatic carboxylate groups were to dissociate from the PVC molecules, abstracting methylenic hydrogen atoms to form acid molecules as in Equation 18.



$$-\mathrm{CH{=}CH{-}}\underset{\underset{\displaystyle\mathrm{RCOO}}{|}}{\mathrm{CH}}\mathrm{{-}CH_2{-}CHCl}- \longrightarrow -\mathrm{CH{=}CH{-}CH{=}CH{-}CHCl}- + \mathrm{RCOOH} \qquad (18)$$

Then new double bonds would be formed to stimulate allylic dehydrochlorination. Thus, although the carboxylic acid molecules would be able to react with basic lead stabilizer to regenerate intermediate lead carboxylates for stabilization, the dehydrochlorination would proceed at some uniform (zero order) kinetic rate with the development of conjugated polyenes giving colour. This would conflict with the research described in Sections 4.2 and 4.3 which shows that dehydrochlorination is retarded, and with independent work [4, 46] which shows that development of colour is restricted, by lead stabilizing systems in hot PVC.

Hence another kind of stabilizing mechanism has been devised, based on the free radical chain dehydrochlorination process for PVC [30] (Section 4.4.1.3), and this has been called "true stabilization" [15–17].

4.5.2. True stabilization theory

The essential features of true stabilization involving basic lead carbonates in PVC may be summarized as follows.

First, reaction occurs between the basic lead carbonate and stearic acid (which may be used as a lubricant in plasticized or rigid PVC) [15–17], or between the hydrated basic lead carbonate and hot DOP in plasticized PVC [22], giving carboxylates of lead which may be basic or neutral salts depending on the relative concentrations.

Second, these carboxylates of lead take part in exchange reactions with chlorine atoms, released from the decomposing PVC as depicted by Equation 7 in Section 4.4.1.3, to give basic or neutral chlorides of lead and carboxylate free radicals (groups with unpaired electrons). For neutral lead stearate the exchange could be written as in Equation 19:

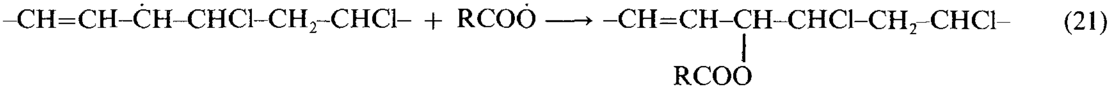
$$\dot{C}l + 0.5[Pb(C_{17}H_{35}COO)_2] \longrightarrow 0.5[PbCl_2] + C_{17}H_{35}CO\dot{O} \qquad (19)$$

whilst for ANLOP the exchange reactions could be written as in Equation 20:

$$\dot{C}l + 0.5[PbC_6H_4(COO)_2] \longrightarrow 0.5[PbCl_2] + 0.5[C_6H_4(CO\dot{O})_2] \qquad (20)$$

In this way the chlorine atoms are trapped and unable to propagate dehydrochlorination in the manner depicted by Equation 6.

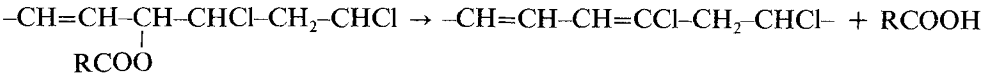
Third, the carboxylate free radicals esterify PVC macroradicals at carbon atoms with unpaired electrons as depicted by Equation 21:



$$-CH{=}CH{-}\dot{C}H{-}CHCl{-}CH_2{-}CHCl{-} + RCO\dot{O} \longrightarrow -CH{=}CH{-}\underset{\underset{RCOO}{|}}{CH}{-}CHCl{-}CH_2{-}CHCl{-} \qquad (21)$$

so that the unpaired electrons become paired and the stimulus for loss of chlorine atoms from the PVC by the means depicted in Equation 7 is eliminated.

Fourth, the carboxylate groups subsequently dissociate from the PVC chains, taking chloromethylenic hydrogen atoms from neighbouring sites to form acid molecules, and leaving carbon–carbon double bonds with the chlorine atoms in relatively stable vinyl type positions as depicted by Equation 22:



$$-CH{=}CH{-}\underset{\underset{RCOO}{|}}{CH}{-}CHCl{-}CH_2{-}CHCl \rightarrow -CH{=}CH{-}CH{=}CCl{-}CH_2{-}CHCl{-} + RCOOH \qquad (22)$$

Fifth, these carboxylic acid molecules react with unused basic lead carbonate to give more carboxylates of lead. Thus the mechanism is continuous and cyclic, retarding PVC dehydrochlorination whilst the reservoir of crystalline stabilizer lasts. This was found to be so for plumbonacrite which reacted according to first order kinetics during efficient stabilization in plasticized and in rigid PVC with stearic acid as the lubricant [15] (Section 4.2.1).

Sixth, in less favourable circumstances which induce rapid PVC decomposition (such as when heating in air), or in the absence of the relatively mobile aliphatic carboxylate groups, the true stabilizing regime might not be entirely effective and some HCl scavenging may also occur. This was found to be so for various plasticized and rigid PVC samples heated in air [19] (Section 4.1.2).

Seventh, in very favourable cases the true stabilizing regime may retard the PVC dehydrochlorination to almost negligible rates, so that effective stabilization may continue long after the crystalline stabilizer has all reacted, then relying on carboxylates of lead already formed in excess of true stabilizing requirements. This was found to be so for a plasticized PVC sheet milled with a relatively fine particle size hydrocerussite and commercial stearic acid [16, 17] (Sections 4.2.2 and 4.2.3).

4.5.3. General aspects of true stabilization

The foregoing theory of true stabilization was developed from results obtained using basic lead carbonates with stearic acid in PVC. However, there is no reason to think that the same mechanism would not apply to other basic lead stabilizer/aliphatic carboxylate lubricant systems. Indeed the work [19] discussed in Section 4.1.2 and the independent research [46] mentioned in Section 4.5.1 (both on stabilization with tribasic lead sulphate in the presence or absence of stearic acid) indicate this. Thus, the basic lead stabilizer can be regarded as a reservoir of lead oxide which is available to react with aliphatic carboxylic acid added for lubrication or released according to Equation 22 in the true stabilizing mechanism.

It will be evident from the above that the proportions of basic lead stabilizer and of aliphatic carboxylate lubricant determine the period of effective stabilization in PVC. Thus, it is clear from the independent research [42, 46] mentioned in Section 4.5.1 that lead stearate alone would be an effective true stabilizer. However, this compound has limited compatability with PVC [47], and it would not confer long term stabilization on PVC in a normal formulation. On the other hand, it is possible to add quite large amounts of crystalline basic lead salts which would act as the reservoirs for extended periods of true stabilization [15–17].

5. Conclusions

Both the unimolecular and the ionic mechanisms for PVC thermal dehydrochlorination described in Sections 4.4.1.1 and 4.4.1.2, respectively, can be regarded as single step processes. Also, the popular mechanism which suggests that stabilization occurs by direct replacement of labile chlorine atoms in the polymer chain with other groups as described in Section 4.5.1 must be regarded as a single step process. In contrast, the free radical dehydrochlorination mechanism described in Section 4.4.1.3 is a two step cyclic process. Also, the true stabilizing mechanism described in Section 4.5.2 for lead compounds is a multi-step regenerative process, which does not involve direct replacement of labile chlorine atoms in the PVC with other groups.

As demonstrated in Section 4.5, the regenerative nature of true stabilization involving basic lead compounds and aliphatic carboxylate groups accounts for practical observations which are not explained by the more popular single-step replacement mechanisms. If it were not for the general use of basic lead salts as reservoirs in combination with relatively small amounts of aliphatic carboxylate groups which react with these reservoirs and behave as carriers for the lead, it would be difficult or impossible to derive evidence on which to base a theory such as free radical true stabilization. Here it is useful to consider briefly some more evidence which supports the true stabilization theory.

Transition metal salts are known to catalyse PVC thermal dehydrochlorination. Iron and zinc salts are notorious in this respect and cadmium salts also cause rapid dehydrochlorination [29]. It is generally assumed that these catalytic effects arise from ionic characters in the metal salts accelerating ionic dehydrochlorination by varying degrees. However there is evidence from ESR measurements to show that cadmium stearate accelerates free radical PVC dehydrochlorination [48], and it may be that all transition metal salts catalyse free radical dehydrochlorination perhaps by influencing the rates at which polymerizing free radical initiator residues dissociate from PVC chain ends (as illustrated by Equation 10; Section 4.4.2.1).

By contrast, it was found that PVC stabilized with barium stearate developed lower spin (unpaired electron, or free radical) concentrations than unstabilized PVC during comparable heat treatments [48]. Also, it has been found [49] that dehydrochlorination rates and spin generation rates are retarded in parallel ways when PVC is stabilized with dibutyl tin dilaurate as compared with the unstabilized polymer.

PVC has been found to react with various solvents. In the case of toluene [50], radioactive trace techniques showed that $C_6H_5CH_2$– groups were incorporated into the polymer molecules in direct proportion to the extent of dehydrochlorination. This was explained by exchanges involving chlorine atoms, and the incorporation of the pendant groups, by reactions formally analogous to those depicted in Equations 19 and 21 of Section 4.5.2. In the case of phenolic solvents [51–53], was found that dehydrochlorination was relatively slow with allyl substituted phenols, suggesting that the allylic groups behaved as sinks for chlorine atoms released by free radical decomposition of the PVC.

PVC is found to be stabilized to various extents in mixtures with certain other polymers. In the case of mixtures with polymethylmethacrylate [54–56], the PVC thermal dehydrochlorination was substantially retarded whilst the polymethylmethacrylate decomposition was modified in ways which can be explained only in terms of attack by chlorine atoms. Similar results were obtained for PVC mixed with polystyrene [57]. It is relevant that the PVC–polymethylmethacrylate mixtures showed lower free radical accumulation rates than PVC heated alone under the same conditions [58].

It has been found that PVC thermal dehydrochlorination is markedly retarded by chloromercuryacetaldehyde [59]. It was demonstrated that this effect can be explained only in terms of reactions involving chlorine atoms released by the PVC and which are trapped by the chloromercuryacetaldehyde, thereby reducing the PVC free radical decomposition.

In view of such evidence as just described the true stabilization mechanism discussed in Section 4.5.2 must be regarded as a reasonable (if not perfect) explanation of behaviour. An interesting line of research which might help to confirm this mechanism would be to compare the deleterious effects of various transition metal carboxylates on PVC thermal dehydrochlorination with the beneficial effect of other metal carboxylates including lead stearate (or combinations of basic lead salts with sources of aliphatic carboxylate groups) which are known to be effective stabilizers, using ESR measurements to confirm that the former salts accelerate free radical dehydrochlorination whereas the latter materials retard this process.

Acknowledgements

The author is indebted to the Directors of Associated Lead Manufacturers Ltd within the Cookson Group plc. for encouraging this publication. Sincere gratitude is expressed to Dr J. S. Campbell (Research Manager here) for his constructive criticism of the manuscript, and to Dr E. H. Amstein (formerly Research Manager here) for encouraging investigations on which the true stabilization theory is based. Also, gratitude is expressed to Messrs J. C. Morley, D. Pearson and D. Youd for invaluable discussions on technical aspects of PVC processing and stabilization.

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Received 5 December 1984
and accepted 29 March 1985