Main Functions of Iron Compounds as Smoke Suppressant in Poly(vinyl Chloride) Combustion

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Synopsis

Whatever the state of the iron compounds as smoke suppressant during the combustion of poly-(vinyl chloride), they lead rapidly to native αFe_2O_3 in the char residue left after dehydrochlorination. It causes incandescence of the char residue and catalyzes its oxidation into carbon monoxide and carbon dioxide that contributes to decreasing the amount of available carbon for the soot formation after self-ignition. $FeCl_2$ and $FeCl_3$ are the precursors of αFe_2O_3, which is the true compound as smoke suppressant. Nevertheless, as intermediate, iron chlorides are able to modify the degradation processes, and they favor the formation of light tars instead of heavy tars. For that reason the iron compounds cause the formation of smoke at lower temperature than for pure PVC, but, as αFe_2O_3 is formed, the smoke production levels off and then decreases. The higher the ease of the iron compounds to give chlorides through reaction with HCl and further native αFe_2O_3, the higher the ease of the additive to cause the oxidation of the char residue sooner and in consequence to decrease the smoke level. In the PVC combustion three main steps may be distinguished: dehydrochlorination step between 200–300°C; tars aerosols formation from the char residue between 300°C and self-ignition; at temperature higher than self-ignition, formation of soot from the previous tars as precursors.

INTRODUCTION

Iron compounds are well known as smoke suppressants in combustion of rigid poly(vinyl chloride) (PVC) and are efficient under mineral forms (oxides, chlorides, nitrates, $\cdots$[1]) as well as organometallic forms (ferrocene,[2,3] acetylacetonate, $\cdots$[1]). They cause incandescence of char residue left after dehydrochlorination in the range of temperatures 350–450°C. This phenomenon parallels quantitative carbon monoxide and carbon dioxide formation whereas such products are normally formed at temperatures higher than 500°C for pure PVC.

Furthermore, in a previous study[3] it has been shown that, in the presence of HCl generated by PVC degradation in air, oxidation of ferrocene really occurs up to the final αFe_2O_3 state that suggests the active species as smoke suppressant are not the additives under their initial form but the products of reaction with HCl. Then the main purpose of this paper is to characterize the active species in the different phases of PVC combustion (dehydrochlorination, burning in smoldering or in flaming conditions) to obtain a better understanding of their behavior in the oxidation reactions.

EXPERIMENTAL

All iron compounds studied (Fe_2O_3, $FeCl_3$, $FeCl_2$, 4 H_2O, ferrocene Fe 55) and

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iron acetylacetonate are commercial products without further purification.

The experiments were carried out using bulk PVC supplied by Rhone Poulenc.

Mixtures with additives were obtained as powders mixed with an electric mill. The amount of additive was generally 1.5 g/100 g resin and sometimes higher for Mössbauer analysis (6 wt %).

The experimental method to assess the smoke level from PVC was roughly similar to the method used previously according to the AFNOR test T5 1073.[1,3,4] Basically the sample is rapidly introduced using a magnetic device into a quartz tube, itself inside a tubular oven (opening oven Heraeus) previously heated at a fixed temperature and flowed with an air stream of 120 L/h, which drives the aerosols to an optical device where the obscuration of a light beam is measured continuously across a path between a light source and a photocell. Thus the optical density $\log I_0/I$ to was measured between 0 and 4 decades and recorded against time. The area S under the curve represents the total amount of smoke produced.

The formation of oxidation products such as carbon monoxide and carbon dioxide is followed continuously using two gas analyzers (Cosma Apparatus Type Rubis 3000) in line after the furnace and calibrated for these two gases. The curves representing CO and CO_2 evolution against the time are recorded, and the total amount of CO and CO_2 evolved is calculated from the area under these curves.

The transformation of the iron compounds in the different steps of the PVC combustion has been studied using Mössbauer analysis. As described previously, the PVC samples are put inside the tubular oven, but the combustion is stopped after intervals of time between 20 and 300 s by introducing nitrogen instead of air flow and meantime taking rapidly the samples outside of the heating zone to be cooled down. The PVC samples after combustion were put between two mica sheets pressed at 1 ton/cm^2 and then put inside a duraluminium cell.

Nuclear gamma resonance (NGR) absorption spectra were obtained by using a constant acceleration driving unit (Numelec), operated in the triangular mode, slaved to a 1024-channel analyzer (Elscint). γ rays from a 100 mCi ^{57}Co/Rh (Amersham) source were detected by an 0.1 mm thick NaI scintillation probe (Elscint). Calibration was achieved from the Fe metal absorption spectrum. After computer folding, the decomposition of spectra was performed, and the Mössbauer parameters were determined by using the program Mosfit,[5] assuming a Lorentzian shape of the lines. Isomer shifts (IS) in this paper are relative to sodium nitroprusside and given with a precision of ±0.03 mm/s as for quadruple splittings (QS) and experimental line widths W. After Mössbauer analysis, chlorides in the char residue are extracted using heated water (80°C) and titrated using a coulometric method.[6]

The rate of transformation of the iron compound during PVC combustion is calculated through the ratio of $FeCl_3$ assessed from chlorides titration to the theoritical $FeCl_3$, which may be formed through reaction with HCl.

RESULTS AND DISCUSSION

Figure 1 shows typical dynamic curves for the obscuration and the production of CO and CO_2, respectively. The quantitative data for the smoke level and for
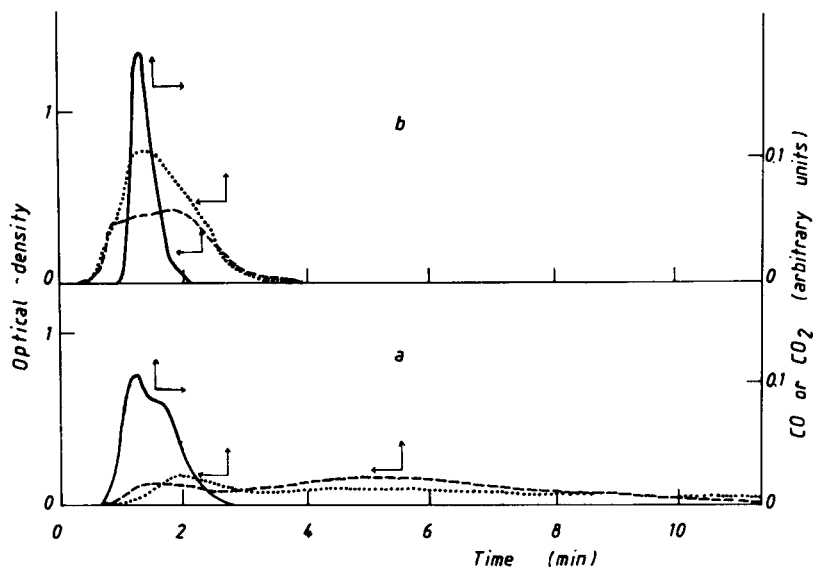
Fig. 1. Obscuration curves (——) and CO (- - -) and CO_2 ($\cdots$) evolution in smoldering conditions (565°C) for PVC (50 mg) without (a) or in the presence of Fe_2O_3 (1.5 wt %).

the two previous gases evolved during the combustion are calculated from the area under the curves and the influence of the following additives, Fe_2O_3, ferrocene, $FeCl_2$, and $FeCl_3$, with respect to the temperature is shown Figures 2–6. Incandescence is observed at various temperatures between 350°C and 500°C according to the nature of the additive.   The greatest amount of smoke is formed
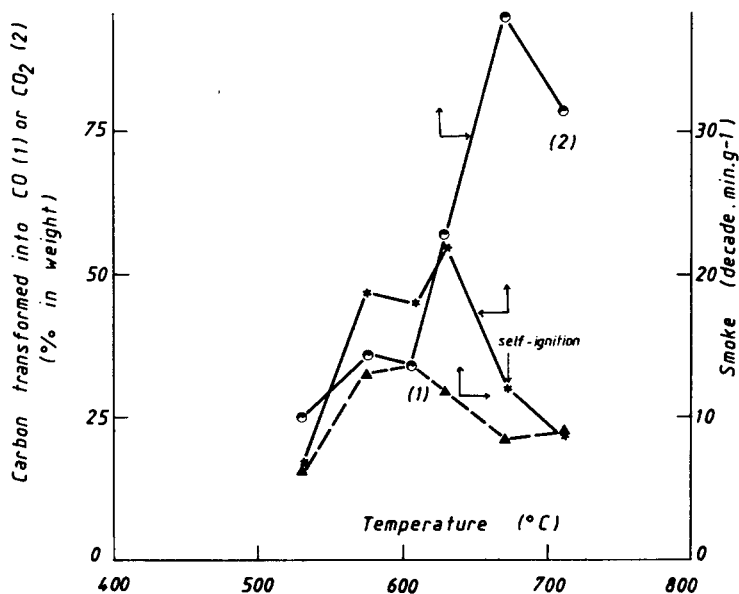
Fig. 2. Smoke level (✱) and carbon converted into CO (▲) and CO_2 (●) for pure PVC (50 mg) vs. temperatures of combustion.
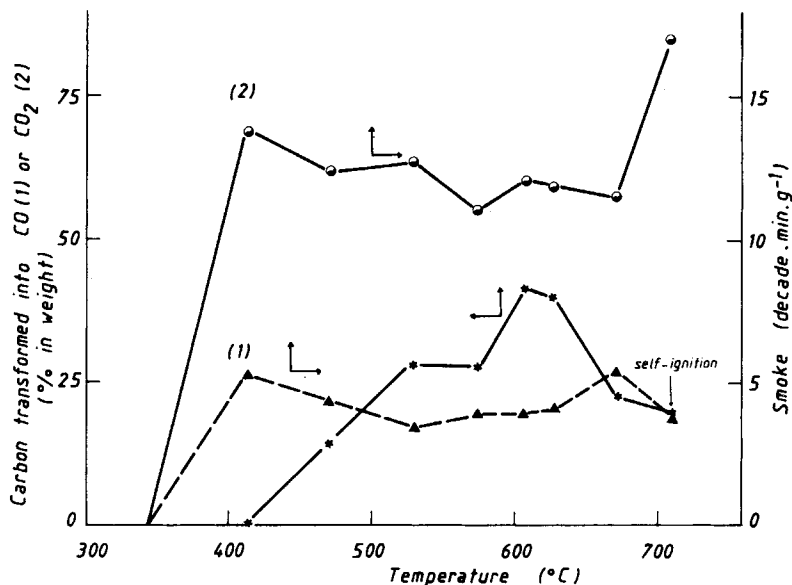
Fig. 3. Smoke level (∗) and carbon converted into CO (▲) and CO_2 (◒) vs. temperature of combustion for PVC (50 mg) in the presence of ferrocene (1.5 wt %).

at about 620°C, 60°C below the self-ignition temperature of PVC (680°C in our experimental conditions).

At temperature higher than 500°C (smoldering or flaming conditions) most of the additives cause a decrease of the smoke level, but at temperatures lower than 500°C (smoldering conditions only) all the iron compounds enhance the smoke level with respect to the pure PVC as the oxidation of the char residue left after dehydrochlorination. $FeCl_3$ is able to initiate the formation of smoke
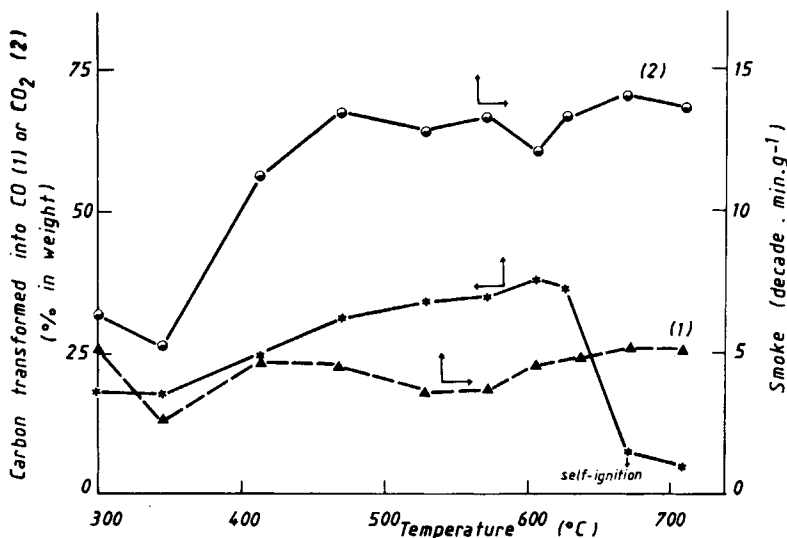

Fig. 4. Smoke level (∗) and carbon converted into CO (▲) and CO_2 (◒) vs. the temperature of combustion of PVC (50 mg) in the presence of $FeCl_3$ (1.5 wt %).
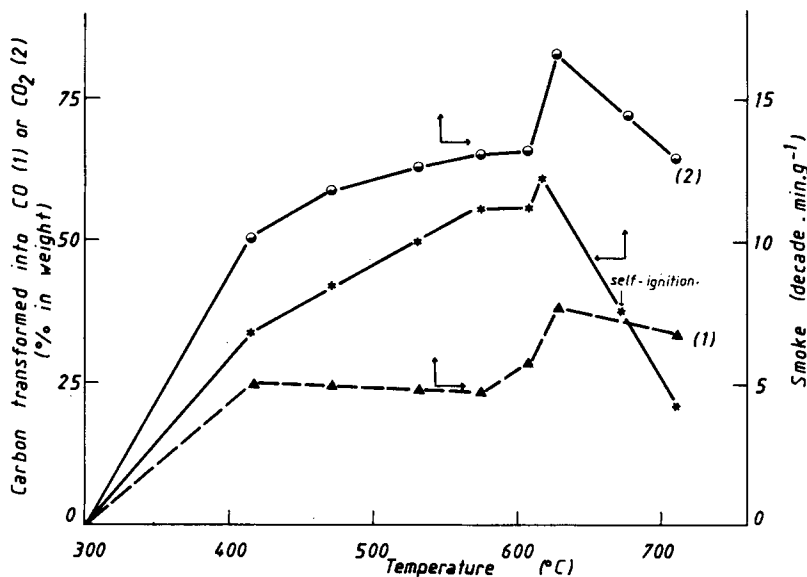
Fig. 5. Smoke level (∗) and carbon converted into CO (▲) and CO_2 (◉) vs. the temperature of combustion for PVC (50 mg) in the presence of $FeCl_2$ (1.5 wt %).

at temperature lower than 300°C, is a very efficient oxidation catalyst mostly at rather low temperature, and also causes the PVC oxidation at temperatures lower than 300°C, although the dehydrochlorination is not yet completely finished.

To study the transformation of the iron additives during PVC combustion, a set of experiments were carried out at 450°C in smoldering conditions but in presence of 6 wt % of the additives to have enough sensitivity for the Lamb–
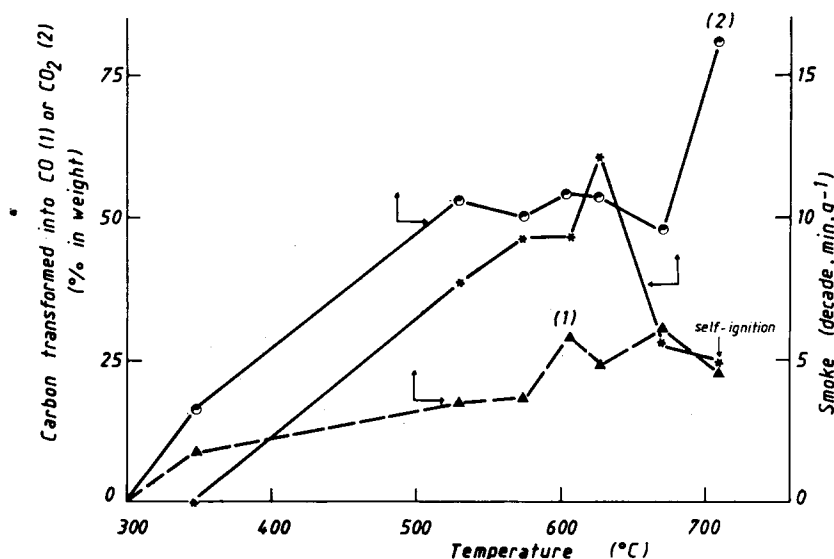

Fig. 6. Smoke level (∗) and carbon converted into CO (▲) and CO_2 (◉) vs. the temperature of combustion for PVC (50 mg) in the presence of Fe_2O_3 (1.5 wt %).
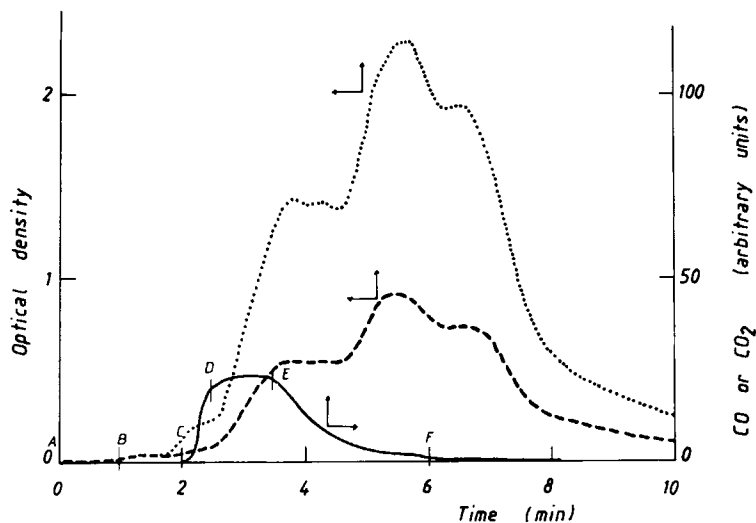
Fig. 7. Obscuration curves (——) and CO (- - -) and CO_2 ($\cdots$) evolution during PVC combustion in smoldering conditions (450°C) and in the presence of Fe_2O_3 (6 wt %). Sample weight 750 mg.

Mössbauer parameters determination. Figure 7 shows the obscuration curve and the carbon dioxide and carbon monoxide evolution vs. the time for Fe_2O_3. The smoke formation appears after an induction time of 2 min (C) as increases in CO_2 and CO evolution are already detected after 1 min (B) while 20% of Fe_2O_3 is transformed into $FeCl_3$, identified through a coloration test in the presence of potassium thiocyanate (red color) and assessed through the coulometric
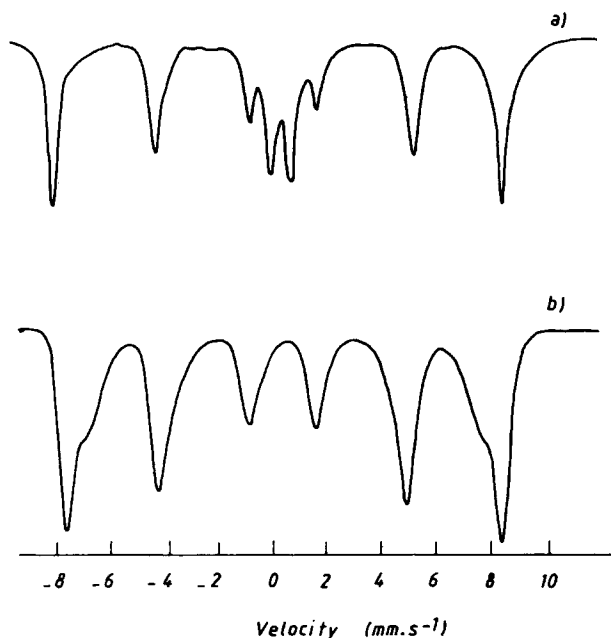

Fig. 8. Mössbauer spectra of the char residue left after combustion at 450°C in the presence of Fe_2O_3 for: (a) 2 min (point C, Fig. 7); (b) 6 min, 20 s (point F, Fig. 7).
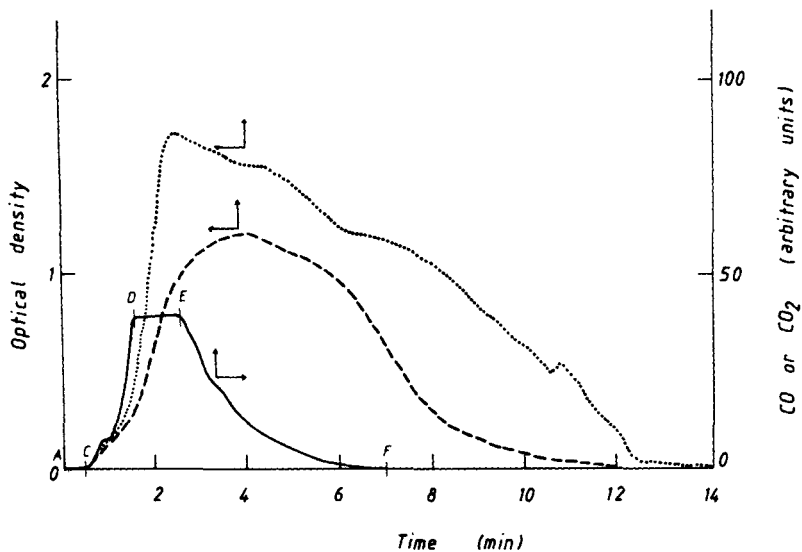
Fig. 9. Obscuration curve (—) and CO (- - -) and CO_2 ($\cdots$) evolution during PVC combustion in smoldering conditions 450°C and in the presence of $FeCl_3$ (1.5 wt %). Sample weight 750 mg.

method. After 2 min (C), $FeCl_3$ is characterized in the char residue by Mössbauer spectroscopy [Fig. 8(a), isomer shift IS = 0.600 mm·s^{-1} and quadrupole splitting QS = 0.617 mm·s^{-1}][7] and represents about only 10% of the initial amount of Fe_2O_3. But after 2 min and 30 s (D), all the iron is in αFe_2O_3 state as in E, the beginning of the smoke reduction, or in F, the end of the smoke formation. αFe_2O_3 is characterized by its typical Mössbauer spectrum with six visible lines with IS = 0.68 mm·s^{-1}, QS = −0.19 mm·s^{-1}, and H = 513 KOe[7] [Fig. 8(b)] and by its isomer shift IS = 0.68 mm·s^{-1}. Furthermore, it is interesting to observe that the smoke formation levels off with the increasing of CO and CO_2 evolution, which remains rather a long time after the end of smoke formation. These results prove that αFe_2O_3 catalyzes the char residue oxidation.
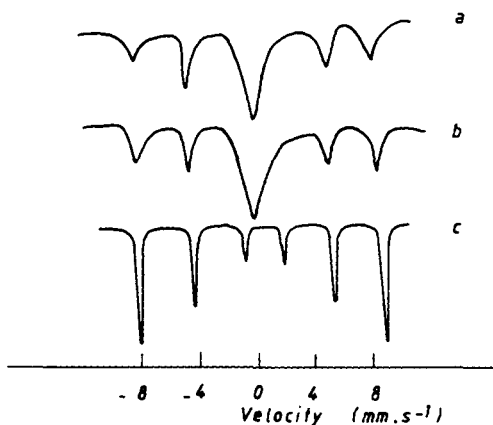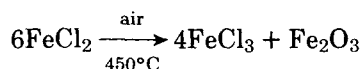

Fig. 10. Mössbauer spectra of the char residue left after combustion at 450°C: (a) 90–150 s in the presence of $FeCl_3$ (1.5%); (b) 60–150 s in the presence of $FeCl_2$ (1.5%); (c) when the smoke production is stopped (point F, Fig. 9).

Iron additives such as $FeCl_3$ and $FeCl_2$ are able to initiate the formation of smoke at a lower temperature than for pure PVC or PVC in presence of Fe_2O_3. They shorten the induction time AC (Fig. 7) before the smoke formation, 30 s for the former and 0 s for the latter, but the shapes of the obscuration curves and the CO and CO_2 curves are the same (Fig. 9). As previously observed with Fe_2O_3, the smoke reduction is concomitant with the evolution of CO and CO_2. From D (90 s for $FeCl_3$ and 60 s for $FeCl_2$) Mössbauer analysis of the char residue shows that $FeCl_3$ and $FeCl_2$ are partly transformed into αFe_2O_3 [Figs. 10(a) and 10(b)], but, when the smoke formation is stopped (F), all the iron in the char residue is in αFe_2O_3 state [Fig. 10(c)]. After 30 s (C) about 35% of the $FeCl_3$ is transformed into αFe_2O_3, which proves that its oxidation is rapid, but after 90 s its presence is still observed [Fig. 11(a)]. Besides, it is interesting to observe [Fig. 11(b)] the presence of $FeCl_3$ (IS = 0.600 mm·s^{-1} and QS = 0.616 mm·s^{-1} in (D) for the $FeCl_2$ additive (IS = 1.45–2 mm·s^{-1} and QS = 1–3 mm·s^{-1} according to literature data). This observation proves that $FeCl_2$ is oxidized into $FeCl_3$, probably according to the following reaction[8]:

$$6FeCl_2 \xrightarrow[450°C]{air} 4FeCl_3 + Fe_2O_3$$

Such a reaction contributes to maintaining a higher concentration of the chlorides in the polymer during the dehydrochlorination step with respect to $FeCl_3$, which is rapidly transformed into Fe_2O_3 as previously shown, but it contributes also to leading to αFe_2O_3 sooner.
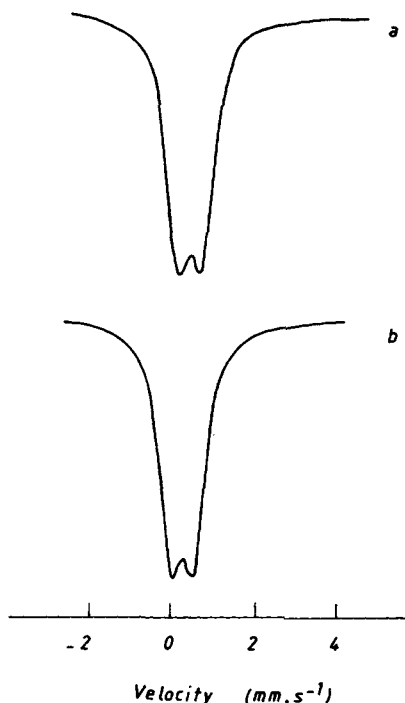

Fig. 11. Mössbauer spectra of the char residue left after combustion at 450°C: (a) for 90 s in the presence of $FeCl_3$ (point D, Fig. 9); (b) for 60 s in the presence of $FeCl_2$ (point D, Fig. 9).

The difference in behavior between Fe_2O_3, on the one hand, and $FeCl_3$ and $FeCl_2$ on the other hand, toward the induction time of smoke formation and carbon monoxide–carbon dioxide formation may be explained on the basis of the work presented by Iida and Goto,[9] who have shown that iron chlorides are among the strongest catalysts for the PVC degradation. Furthermore, they modify the distribution of aromatics and aliphatics in the volatile products evolved during the PVC degradation. In the presence of $FeCl_3$ the volatile products contain about 55% of aliphatics and 29% of aromatics. On the contrary, Fe_2O_3 favors aromatics formation (61% instead 30% for aliphatics). So iron chlorides modify the degradation process of PVC favoring aliphatics, which are easily oxidized, but also the formation of light tars which volatilize as aerosols more easily than heavy tars constituted by polyaromatics, as may be suggested for Fe_2O_3. As shown previously, the obscuration in smoldering conditions is caused by the tar aerosols coming from the char residue pyrolysis.

Because of their prodegradant activities during the processing operations the iron compounds cannot be introduced in the industrial recipes for building under a mineral state. Thus it may be interesting to use iron as organometallic compounds to decrease and even to mask its catalytic action with respect to dehydrochlorination. Furthermore, an organo-iron may be easily dispersed in the polymer matrix. Ferrocene, as a sandwich complex of iron with cyclopentadiene has these two properties, although it reacts with HCl to produce ferrous and ferric chlorides from 200°C. At temperatures, above 400°C it is transformed into αFe_2O_3 state, which enhances the oxidation of the char residue left after dehydrochlorination.[2,1]

In the same line iron acetylacetonate may be used, and Figure 12 shows its role on the smoke as carbon monoxide and carbon dioxide evolution vs. time. There
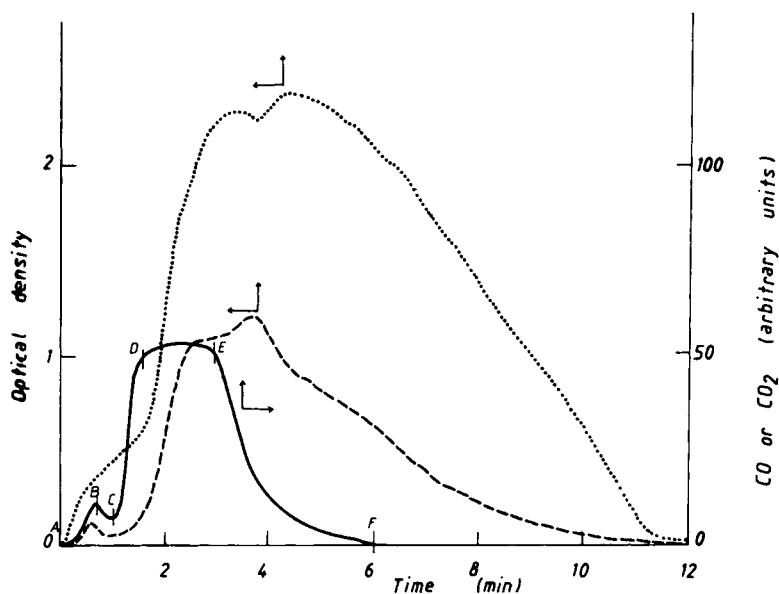

Fig. 12. Obscuration curve (——) and CO (- - -) and CO_2 (· · ·) evolution during PVC combustion in smoldering conditions (450°C) in the presence of iron triacetylacetonate (6 wt %). Sample weight 750 mg.

is an induction time as observed in the presence of Fe_2O_3 or $FeCl_3$, although there are two waves of smoke of unequal importance, the first one being very small with respect to the second. The transformation of the iron acetylacetonate in the different steps of PVC combustion at 450°C and marked by letters on the obscuration curve (Fig. 12) has been followed using Mössbauer analysis and the data are given Table I and Figure 13. It is difficult to identify the nature of the compound containing Fe^{+++} because the absorption of the central peak may correspond to pure iron acetylacetonate, or to iron trichloride, or to the product of thermal decomposition of the iron acetylacetonate, or to new organoiron species (mono, dichloro, $\cdots$ derivatives) (Fig. 14). Nevertheless, the presence of $FeCl_3$ in the char residue has been proved through coloration test in the presence of potassium thiocyanate and using coulometric titration. The chlorides formation (Fe^{++} and Fe^{+++}) is observed after 30 s (B) and their concentration is highest after 90 s (D) and corresponds to about 9% of the initial iron. The formation of αFe_2O_3 is also rapid and this compound appears in the char residue after 90 s (spectrum D, Fig. 12), where its six absorption lines are visible. In the same time carbon monoxide and carbon dioxide evolution strongly increase that confirms the central role of αFe_2O_3 as an oxidation catalyst of the char residue left after dehydrochlorination of the PVC. Furthermore, the smoke formation decelerates after 90 s of heating and is stopped after 6 min, when all the iron occurs in the αFe_2O_3 state (spectrum F, Fig. 13). The carbon dioxide and monoxide evolution continues a long time after the end of the smoke formation, which corresponds to the highest rate of the formation of these oxidation products.

In conclusion, the previous studies show the central role of iron chloride during the dehydrochlorination of PVC, which is the first step of its combustion. The greater the efficiency of the iron additives to give chlorides through reaction with HCl and further transformation in αFe_2O_3 state, the higher the ease of the additive to reduce the smoke formation. Iron chlorides enhance the smoke formation at temperatures below the minimum temperature for observation of smoke for pure PVC because they modify the processes of PVC degradation. They favor the formation of aliphatics with respect to aromatics, and, in consequence, they favor the formation of light tars, which may be volatilized as aerosol at temperatures lower than the heavy tars produced owing the PVC degradation without the presence of additives. In the presence of air, oxidation of the iron chlorides readily occurs up to the final αFe_2O_3 state which plays a central role

TABLE I

Mössbauer Data during PVC Combustion in Smouldering Condition (450°C) and in Presence of Iron Acetylacetonate (6% in Weight)

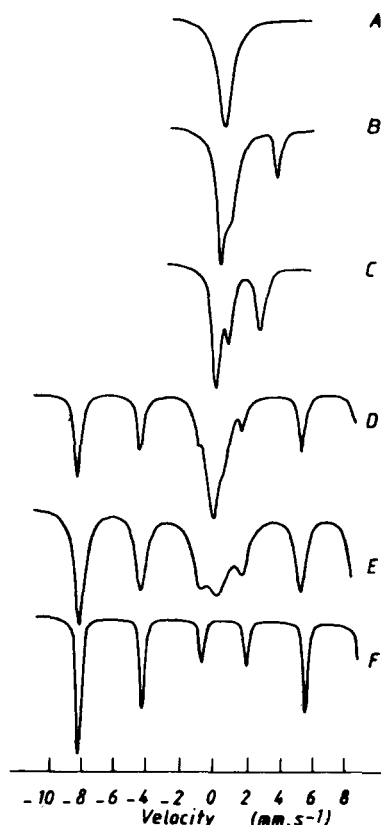| Spectra of Figure 13	Combustion time (s)	Fe^{+++} (central peak absorption) (%)	IS $(mm \cdot s^{-1})$	QS $(mm \cdot s^{-1})$
A	0	0.65	0.434	−0.005
B	30	1.5	0.610	0.545
C	50	2.4	0.623	0.603
D	90	3.2	0.477	0.505
E	180	1.9	0.470	0.003
F	360	αFe_2O_3 (magnetic field: 513 kilo oersted)	0.680	−0.185

Fig. 13. Mössbauer spectrum evolution of the char residue left after combustion at 450°C in the presence of iron triacetylacetonate vs. time (letters refer to Fig. 12).   (A) 0; (B) 30 s; (C) 50 s; (D) 90 s; (E) 180 s; (F) 360 s.

in the second step of PVC combustion before self-ignition.   As an oxidation catalyst of the char residue left after dehydrochlorination, αFe_2O_3 enhances strongly the percentage of carbon oxidized into CO and CO_2 state with a ratio of CO_2/CO always larger than 1 and so contributes to decrease the soot formation
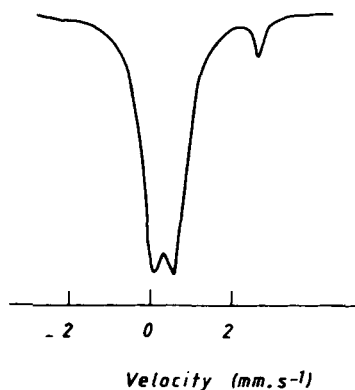

Fig. 14. Mössbauer spectrum of the iron triacetylacetonate heated 20 s at 450°C under nitrogen.

after self-ignition.   The smaller efficiency of αFe_2O_3 as oxidation catalyst of tars in smoldering conditions compared with CuO may be explained partly through the easier volatilization of the latter compounds as aerosol with tars[10,11] and through the higher ease of $CuCl_2$ to be converted into CuO state in the presence of air at moderate temperatures.[12]   The main function of iron compounds as smoke suppressants through native αFe_2O_3 as an oxidation catalyst of the char residue left after dehydrochlorination and of the tars confirms our previous picture for the PVC combustion in three steps: dehydrochlorination, char residue pyrolysis, and volatilisation as tars aerosol and soot formation from the tars after self-ignition.

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