

Tris-(2, 4-Pentanediono) Chromium III – a Fire Retardant Smoke Suppressant for Plasticized Poly(Vinyl Chloride)

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ABSTRACT

A majority of smoke suppressants used for Poly(vinyl chloride) are compounds of metals. Transition metal complexes have been used for quite some time as fire retardant smoke suppressants (FRSS) for Poly(vinyl chloride). Use of Tris-(2,4-pentanediono) chromium III has been examined as FRSS in PVC. The effectiveness of the FRSS is described in terms of various fire properties, namely, smoke release, flammability, time of ignition, heat release and generation of combustion products using a cone calorimeter and Limiting Oxygen Index apparatus. It was found effective at 1 phr in plasticized Poly(vinyl chloride).

KEY WORDS: Poly(vinyl chloride), fire retardant, smoke suppressant, fire properties, Cone Calorimeter, Limiting Oxygen Index.

INTRODUCTION

Extensive use of plastics has accentuated the problem of fire and smoke. Plastics being combustible in nature burn rapidly and produce copious amount of smoke. Poly(vinyl chloride) is one of the major plastics used all over the world. It finds a wide range of applications in industrialized fields, notably in buildings because of its many outstanding properties. Although it is intrinsically flame retardant, large quantities of smoke and toxic gases are evolved when it is forced to burn¹. It is now recognized that smoke is the major problem for both plasticized and unplasticized poly(vinyl chloride). Smoke poses a danger to human life, particularly in the initial phase of a fire, due to reduction in visibility. This can lead to panic and irrational behaviour which makes escape difficult leading to in-

creased number of fatal casualties.

Comprehensive reviews on smoke suppression of polymeric materials have been published^{2,3}. Smoke inhibition of polymers is achieved through use of fillers, additives, surface treatments and structural modifications. Of the large number of suppressants suggested in the literature, it is the reactive additives that form the most widely applicable and diverse group and include oxides of transition metals e.g. MoO₃, V₂O₅, Cu₂O, ZnO, iron as oxides, hydroxides and in powder form, cyanides and thiocyanates of copper, modified antimony oxide and bimetallic compositions of zinc and magnesium as some of the smoke inhibitors used in PVC²⁻⁶. They function both in gas and condensed phase processes, including catalysis of soot oxidation, char formation and changing the nature of pyrolyzates.

Dicyclopentadienyl iron (Ferrocene) was the

first metal based organic (MBO) complex which was widely acknowledged as a fire retardant smoke suppressant for Poly(vinyl chloride)⁷. It increases char formation suggesting involvement in condensed phase. Its application is, however, limited because of high vapour pressure and colour. Also claimed effective was vanadium(III) acetylacetonate, which could be used in either rigid or flexible PVC⁴. Since the majority of known smoke retarders for PVC are compounds of transition metals their ability to participate in redox reaction may be important in smoke suppression. The other important factors are particle size, dispersion characteristics and concentration³. Several flame retardants increase the amount of smoke and toxic gases generated by plastics, if they burn⁸. Smoke suppression at the cost of increase in burning characteristics is not desirable. To achieve an overall improvement in the fire performance, development of fire retardant smoke suppressants (FRSS) is an obvious consequence. Metal based organics cause incandescence of char residue left after dehydrochlorination in the temperature range of 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 PVC⁹. Tris-(2,4-Pentanediono) chromium III; a MBO; was used as FRSS in the present study.

Polymer combustion involves thermal degradation of the solid matrix to gaseous and liquid components. The gaseous components include combustion gases and smoke. Smoke is a dispersion of solid and liquid particles in a carrier gas consisting of combustion products. Solid smoke constituents, particularly in the form of soot, are formed at higher temperatures in the absence of sufficient oxygen. Hirschler¹⁰ reported detailed stages involved in polymer decomposition and combustion (Fig. 1).

The zone corresponding to the formation of volatile decomposition products from the semi-decomposed substrates is the interphase where the reaction of FRSS additives takes place, thereby suppressing the formation of smoke.

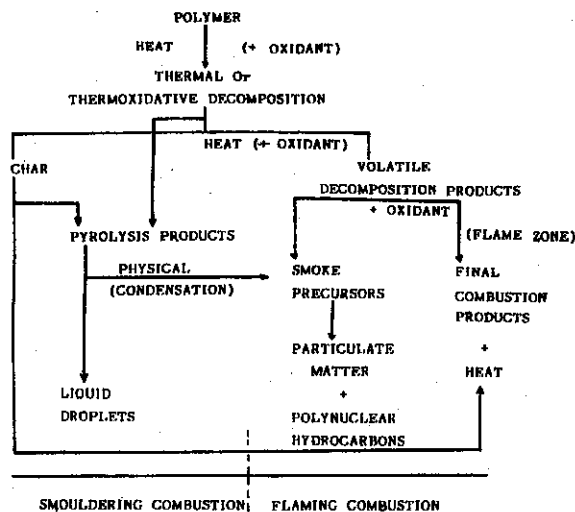


Fig. 1. Polymer decomposition and combustion.

EXPERIMENTAL

Materials

Materials used were of Japanese make unless specified: Virgin poly (vinyl chloride) resin having a degree of polymerization of 1300, VCM less than 0.1 ppm and T.G. of 78°C (Sinetsu Chemical K.K.). Dioctyl Azelate, 'Sansosizer DO', molecular weight 413 and sp gr 0.196 (Shinohon K.K.). Lead complex 'Stabinex TCA' having chemical composition 3 PbO · PbSO₄ · H₂O-Pb 87%, SO₃ 8% and sp gr 7.1 (Mizusawa Chemical). Dibutyl tin dilaurate, 'Stann BI', sp gr 1.05, M.P. 20–26°C. Stearic acid (Merck, Germany). Magnesium Hydroxide, 'KISMA 5A', Specific surface area 8.0 M²/g and particle size 0.6–0.8 μm (Kyowa Chemical), and Calcium carbonate, 'Makuenka CC-R', particle size 0.08 μm (Sirajshi Kogyo K.K.).

PROCEDURE

Tris-(2,4-Pentanediono) chromium III was synthesized using merck chemicals by standard method¹¹ and used as FRSS for plasticized PVC. Chemical compositions as per Table 1 were used for making PVC samples. A two-roll mill having 150 mm dia rollers was used for blending and milling at 165–170°C. This was followed by molding the material into sheets of 300 mm × 150 mm × 1 mm using compression molding at 175°C followed by slow cooling. The preheating time was five minutes. Specimens were cut from the molded sheets (100 mm × 100

mm) for calorimetric studies using a cone calorimeter and (5 mm × 100 mm) for flammability assessment using a limiting Oxygen Index Apparatus. All the specimens were conditioned to constant weight at 23 + 2°C and 50 + 5% RH. All the conditioned specimens except those for flammability assessment were wrapped in aluminium foil covering the unexposed surface and subjected to test conditions as per International Standardisation Organisation (ISO)¹² in horizontal orientation with a retainer frame. Flammability of specimens was studied in accordance with the ASTM standard method¹³.

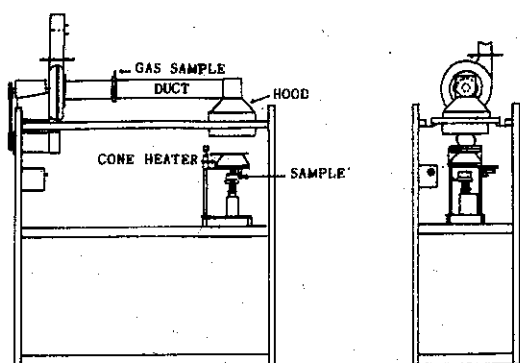


Fig. 2. Overall view of the apparatus

A 'Toyo Seiki' cone calorimeter used (Fig. 2) had a cone heater to provide irradiance levels of 10–110 KW/M². The hood and duct section ensure thorough mixing and enables continuous oxygen sampling and flow measurements—the two measurements essential for estimation of the rate of heat release. Smoke density measurements were made by using helium-neon laser beam across the duct. Combustion products were estimated with the help of different gas analyzers. A 'Stanton Redcroft' FTA-Oxygen Index Apparatus was used for the flammability studies at room temperature.

RESULTS AND DISCUSSION

Specimens of plasticized PVC were prepared by using the recipe given in Table 1. A commercially available fire retardant (FR) PVC was used for comparison. Specimens were exposed to the irradiance levels of 30 and 40 KW/M² in a cone calorimeter and at room temperature in FTA. Effect of FRSS was studied on the burning characteristics and combustion products. The mixture of combustion gases was analyzed in the duct section of the calorimeter and the peak values are reported.

TABLE 1. Recipe for PVC Compositions

PVC	= 100 phr	Diocetyl azelate	= 40 phr
DBTDL	= 0.5 phr	Pbx(SO ₄) _y	= 3.0 phr
Stearic acid	= 0.1 phr		

Set	Composition	Mg(OH) ₂	CaCO ₃	FRSS*
SET I				
	1	70	0	0.0
	2	70	0	0.5
	3	70	0	1.0
	4	70	0	2.0
	5	70	0	3.0
SET II				
	6	50	20	0.0
	7	50	20	0.5
	8	50	20	1.0
	9	50	20	2.0
	10	50	20	3.0

Note: All values are in part per hundred parts of resin (phr)
* Fire Retardant Smoke Suppressant Complex.

TABLE 2. Oxygen Index

Set	Composition	FRSS (phr)	LOI
SET I			
	1	0.0	29.55
	2	0.5	29.65
	3	1.0	29.70
	4	2.0	29.80
	5	3.0	29.90
SET II			
	1	0.0	27.00
	2	0.5	27.10
	3	1.0	27.30
	4	2.0	27.70
	5	3.0	28.10

Note: FRSS Fire Retardant Smoke Suppressant System; LOI Limiting Oxygen Index

Burning Characteristics

Characteristics covered included the time of ignition, flammability, heat release rate and total heat release. Flammability was measured in terms of the Limiting Oxygen Index (LOI). The specimens were

ignited by a propane torch. LOI values of different specimens (Table 2) indicate that the flammability of PVC is strongly influenced by the type and amount of filler used. In Set I where 70 phr of $Mg(OH)_2$ was used the Oxygen Index was 29.55 without any addition of the FRSS while for identical conditions except for the filler (50 phr of $Mg(OH)_2$ + 20 phr of $CaCO_3$) the Oxygen Index was lower (27.1) in Set II. $Mg(OH)_2$ acts as a fire retardant

because it releases inert gases which dilute the fuel in gas phase, also the spent $Mg(OH)_2$ has higher heat capacity as compared to the polymer which reduces thermal energy to degrade the substrate¹⁴. Thus as the amount of magnesium hydroxide is greater in Set I it shows a higher LOI. The role of tris-(2,4-pentanediono) chromium III as a fire retardant smoke suppressant is emphasized by the results which indicate a steady increase in the Oxygen

TABLE 3. Time of Ignition and Rate of Burning

Irradiance Level		30KW/M ²			
Set	/Composition	Ignition time (Seconds)	Burning rate (Kg/M ² s × 10 ⁻²)	Heat release rate (KW/M ²)	Total heat release (MJ)
SET I					
	1	94	1.21	140.40	13.52
	2	96	0.97	151.24	13.55
	3	99	—	154.44	14.27
	4	97	1.93	152.24	14.99
	5	106	—	135.59	12.47
SET II					
	6	92	1.28	147.56	15.61
	7	96	1.63	121.57	15.39
	8	98	1.63	118.21	13.81
	9	106	1.87	143.02	14.43
	10	96	1.86	147.66	15.03
	FR PVC	148	—	176.70	8.64
Irradiance Level		40KW/M ²			
Set	/Composition	Ignition time (Seconds)	Burning rate (Kg/M ² s × 10 ⁻²)	Heat release rate (KW/M ²)	Total heat release (MJ)
SET I					
	1	94	1.21	169.62	20.22
	2	96	0.97	180.74	19.33
	3	99	—	182.28	21.36
	4	97	1.93	176.57	20.79
	5	106	—	173.75	15.45
SET II					
	6	92	1.28	170.96	21.99
	7	96	1.63	175.33	21.04
	8	98	1.63	163.99	16.29
	9	106	1.87	169.45	21.65
	10	96	1.86	173.49	21.40
	FR PVC	148	—	165.62	8.02

Index with increase in the phr loadings of the FRSS from 29.55 to 29.9 in case of Set I when $Mg(OH)_2$ was the filler. The increase was more visible (27.1 to 28.1) when the phr of $Mg(OH)_2$ used was lower i.e. in Set II.

Time of ignition is not important for a deterministic scheme for the first item to ignite, but is important for subsequent burning items. External ignition of specimens was accomplished by a spark plug located 13 mm above the centre of the specimen. Results of different specimens (Table 3) indicate that ignition occurred earlier at 40 KW/M^2 than at 30 KW/M^2 . Fire retardant PVC took considerably longer time for ignition to occur. The effect of FRSS on the time of ignition was small.

A load cell having an accuracy of 0.1 g was used to measure the weight loss during burning. The weight loss was used to compute the rate of burning (Table 3). As expected the rate of burning was higher at 40 KW/M^2 . FRSS seems to have influenced the rate of burning of PVC. In Set I when magnesium hydroxide was used as filler along with 0.5 phr FRSS the rate of burning was lowered by 20% and 33% at 30 KW/M^2 and 40 KW/M^2 respectively. At 2 phr loading the rate of burning was further lowered at 40 KW/M^2 (by 43%). The role of $Mg(OH)_2$ as a fire retardant was evident from the burning rate of the control specimens (1 & 6) at both the irradiance levels. An optimum reduction of 45% in burning rate was observed at 1 phr in Set II at an irradiance level of 40 KW/M^2 . Thus the effect of FRSS in lowering the burning rate was more appreciable at higher irradiance level.

Heat release is a fundamental property of fire and should almost always be taken into account in any assessment of fire hazard. Heat Release Rate (HRR) and the Total Heat Release (THR) by the specimens were estimated by the 'Oxygen Consumption Principle'. The results reported in Table 3 represent THR and the HRR of various compositions. In Set I at 30 KW/M^2 THR increased from 13.52 MJ to 15.01 MJ with the increase in FRSS concentration up to 2 phr. In Set II the trend was just the reverse i.e. THR decreased continuously (15.61 to 13.91) with increase in FRSS up to 2 phr and then increased to 15.03 at 3 phr. THR was near-

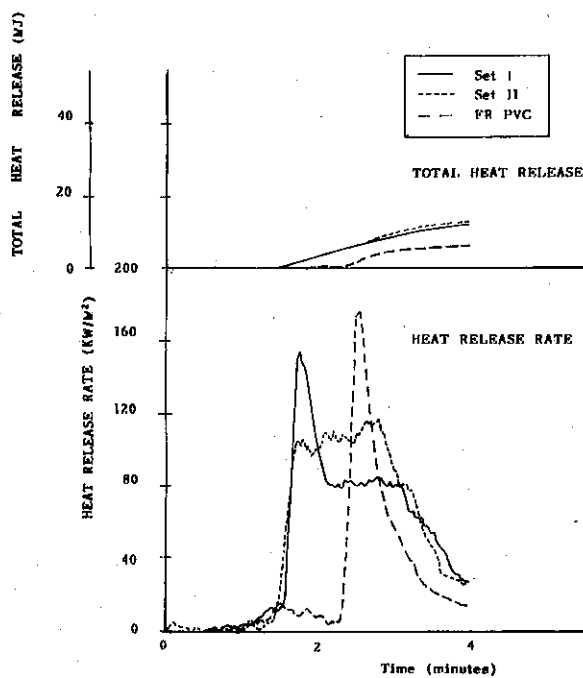


Fig. 3. Comparative heat release (30 KW/M^2).

ly the same between 1 and 2 phr irrespective of the filler used. A similar trend was observed at 40 KW/M^2 though the THR in each case was comparatively higher as expected. In Set II lowest values of THR and HRR were observed for 1 phr of FRSS at both the irradiance levels. It was observed that the type of filler used had an influence on the heat release $CaCO_3$ causing a decrease in HRR and THR; thereby making the material less hazardous. Figs. 3 and 4 show a comparison of HRR and THR between the 1 phr FRSS compositions of Set I and Set II and the FR PVC at 30 and 40 KW/M^2 respectively. The values were higher at 40 KW/M^2 though the trend was similar in both the cases. The peak values of HRR were obtained earlier in case of FRSS modified compositions as compared to the FR PVC. It can, therefore, be concluded that the heat release was relatively lower in case of FR PVC samples.

Combustion Products

The gaseous combustion products monitored

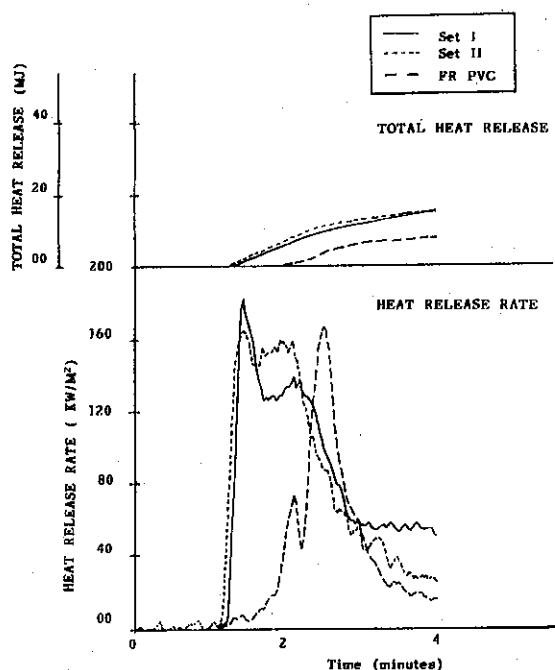


Fig. 4. Comparative heat release (40 KW/M^2).

during combustion of specimens included oxygen, carbon monoxide, carbon dioxide, hydrocarbons and smoke. The yield of combustion gases and smoke density in terms of percentage transmittance, at the two irradiance levels are shown in Table 4.

Carbon monoxide and carbon dioxide levels increased slightly on addition of FRSS because MBOs result in the formation of CO and CO_2 at lower temperatures¹⁰. CO generated was of the order of 100 parts per million (ppm). The variations with respect to the FRSS loading and irradiance levels were insignificant. 250 ppm and 280 ppm of CO were observed in case of FR PVC at 30 and 40 KW/M^2 respectively. Carbon dioxide showed a steady decrease (2165 ppm to 1765 ppm) with the increase in FRSS levels for specimens of Set I, while in Set II a decrease from 2476 ppm to 1784 ppm was observed at 0.5 phr but further addition of the FRSS caused a steady increase in CO_2 level up to 2451 ppm. The increased level of CO_2 in Set II may be attributed to the presence of CaCO_3 as the second filler. The FR PVC produced 2000 ppm

and 1700 ppm of CO_2 at the two irradiance levels. At 30 KW/M^2 the oxygen level first increased from 2010 ppm to 3040 ppm up to 1 phr, and then decreased to 2700 ppm at 3 phr of FRSS for Set I. The trend was just the reverse in case of Set II. However, the variations were minor in both the sets at 40 KW/M^2 . Hydrocarbons showed a minimum value of around 46 ppm at 30 KW/M^2 and 83–92 ppm at 40 KW/M^2 with increase in loadings of FRSS probably because of reduced formation of benzene as an effect of the complex used.

Smoke density was monitored by using He-Ne Laser beam across the duct with a silicon diode photo detector at the other end. Low values of smoke were observed when 1 phr of FRSS was used. At 30 KW/M^2 in Set I the smoke density continuously decreased (by 31%) up to 2 phr followed by a slight increase at 3 phr. In set II decrease was of 16% at 1 phr but a further addition of FRSS caused an increase in smoke density. The maximum smoke suppression at 30 KW/M^2 and 1 phr FRSS in the two sets was 21 and 16%. At 40 KW/M^2 increasing the loading of FRSS caused an increase in smoke density in both the sets except for a small decrease at 0.5 phr in Set I. The complex appears to have altered the course of decomposition of the polymer so that lower amount of volatiles and large quantity of char were formed thereby reducing both the flammability and smoke generation^{2, 4, 6}.

Comparison of the combustion products generated by the 1 phr FRSS specimens of Set I and Set II (which showed lowest values in terms of smoke density) and the FR PVC are given in Figs. 5 and 6 for 30 and 40 KW/M^2 respectively.

Though the peak values of CO, CO_2 and O_2 appear earlier in case of FRSS specimens, they were lower than those for the FR PVC; particularly the CO levels. Hydrocarbons were generated in comparatively huge quantities and at a much earlier time in case of FR PVC and hence lower levels of %T were obtained when FR PVC was subjected to test. For the FR PVC, though all the gaseous products were generated in relatively large quantities, the quantities of hydrocarbons and smoke were significantly higher particularly at the higher irradiance level.

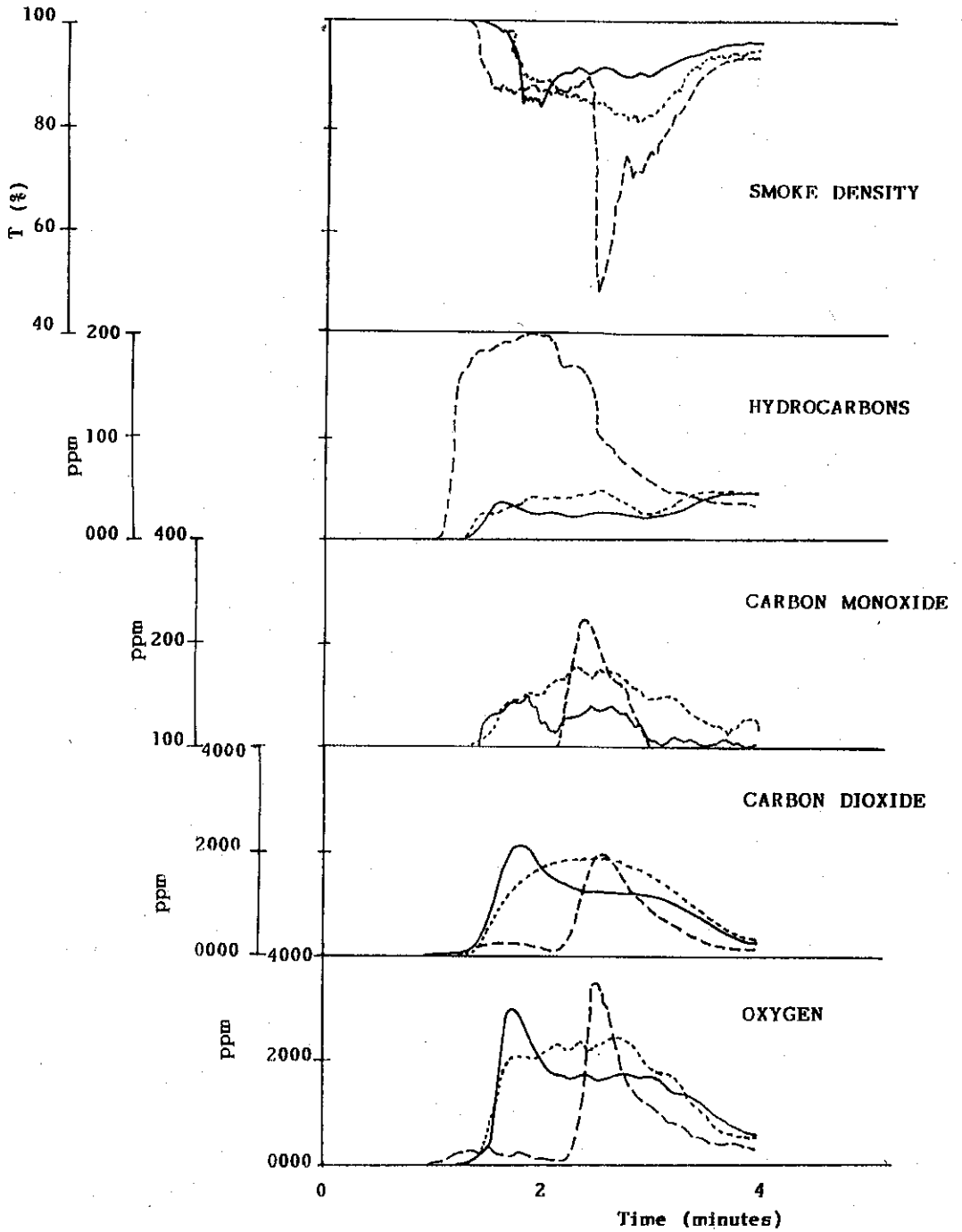


Fig. 5. Comparative combustion products (30 KW/M²).

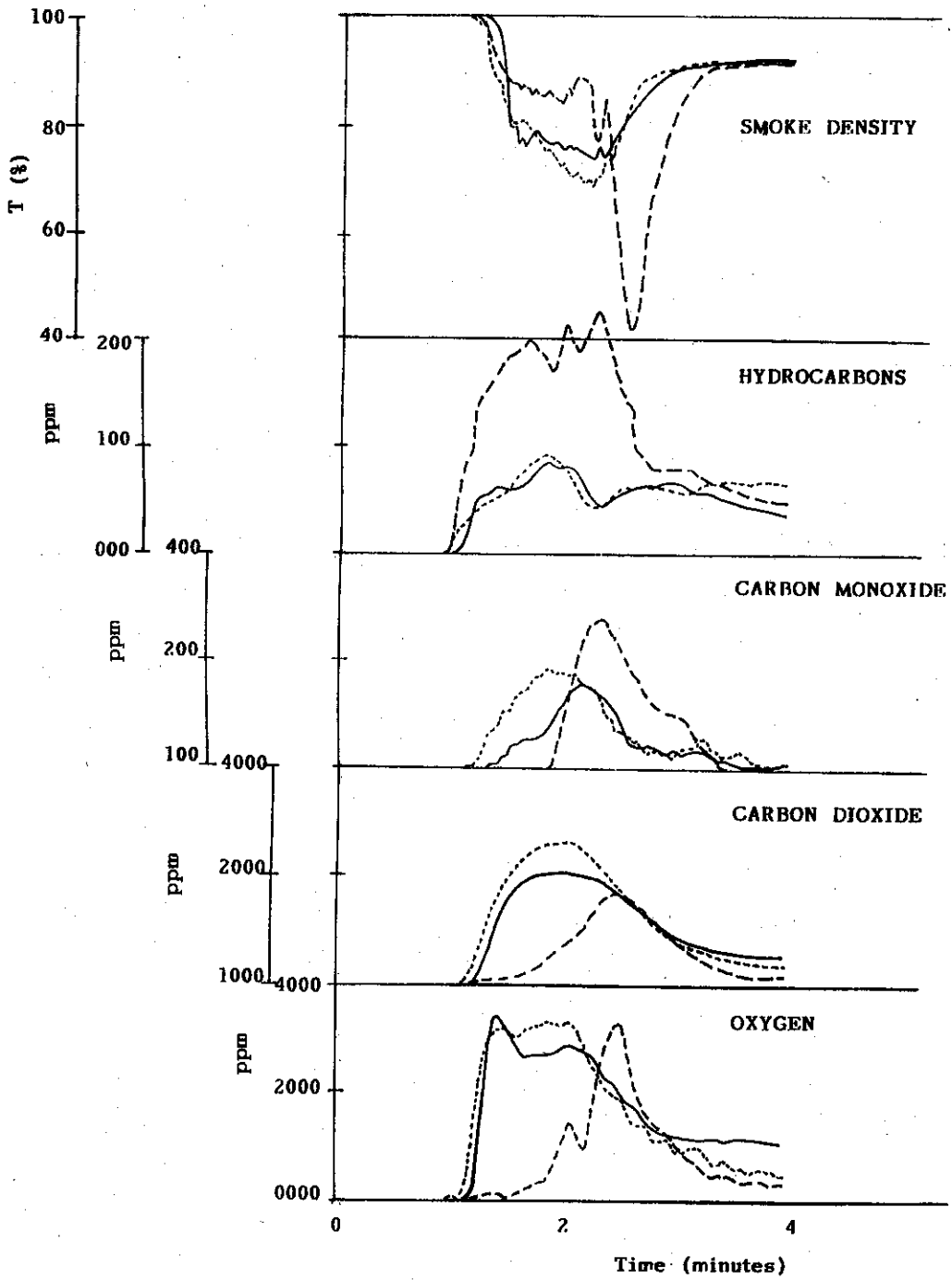


Fig. 6. Comparative combustion products (40 KW/M²).

caused a two-fold increase in heat release it proved effective in generating lower levels of combustion products and up to 4.5 times lower smoke density.

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