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DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH AND FIRE OFFICES' COMMITTEE
JOINT FIRE RESEARCH ORGANIZATION

EXAMINATION OF THE PRODUCTS OF COMBUSTION
OF A CHLORINATED METHYL METHACRYLATE

by

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Summary

An examination has been made of the products of combustion of a chlorinated methyl methacrylate.

Hydrogen chloride, carbon monoxide, and carbon dioxide were present in dangerous concentrations, and there were small amounts of phosgene, which were insignificant compared with the other gases.

Introduction

The use of newer materials such as plastics has made it necessary to consider the possibility that they might evolve especially toxic gases when they became involved in fires.

The combustion of the commoner organic materials such as cellulose is accompanied by evolution of carbon dioxide and carbon monoxide. The products of combustion of materials such as rubber, silk, and wool contain sulphur and cyanogen compounds, (1) and cyanides and ammonia, in addition to carbon monoxide were produced during the combustion of phenolic and melamine resins. (2) Other experiments (3) made in U.S.A. demonstrated that although cyanides were evolved from melamine resins and wool, the toxicity of the combustion products was due almost entirely to carbon monoxide.

Many of the plastics in common use are chlorinated compounds such as polyvinyl chloride, and a chlorinated methyl methacrylate plastic has been introduced with the object of reducing the inflammability of the methacrylate plastic. Fears were expressed that when heated, as in a fire, the material would evolve sufficient phosgene to make the combustion products very toxic. Some experiments have therefore been made to investigate this possibility.

Materials

The experiments were made with a specimen of clear, colourless, chlorinated methyl methacrylate sheet $\frac{3}{16}$ in. thickness from which specimens were cut with a hacksaw.

Preliminary experiments

When the material was held in a bunsen flame white fumes were evolved and the combustion products smelt strongly of hydrochloric acid.

Some combustions were then carried out in an electrically heated tube furnace with an absorption train, and a regulated air flow. They were not successful because a liquid (possibly a monomer) was carried over and interfered with the absorption.

Combustion apparatus

The final form of the apparatus used in the experiments is shown in Fig. 1. Specimens were burned in a porcelain boat carried in a heating coil contained in a 5½ litre flask, which was sealed. During the combustion there was a pressure rise in the vessel, and a rubber balloon was attached to act as a pressure release, and yet prevent loss of gases. Combustions were made over a range of temperatures, and the ratio of air to combustible was varied by using different weights of specimen. After the combustion had finished the apparatus was allowed to cool, and the products of combustion were analysed.

Analytical methods

Total carbon and chlorine

Before burning the specimen a measured volume of standard sodium hydroxide solution was poured into the flask and was afterwards analysed to estimate chloride and carbonate. Comparison of the results with the chlorine or carbon content of the original material gave a measure of the extent of the decomposition of the plastic; any phosgene would be decomposed to hydrogen chloride and carbon dioxide, and would be estimated as such.

Composition of combustion gases

In order to examine the composition of the gases, combustions were made in a dry apparatus with calcium chloride to absorb water which would decompose phosgene. The gases were then analysed, carbon monoxide, and carbon dioxide were determined by the standard methods of gas analysis, chlorine was determined using o-tolidine. (4)

Some difficulty was experienced with the detection and estimation of phosgene. In these experiments it was necessary to determine traces of phosgene in the presence of heavy concentrations of hydrogen chloride and possibly chlorine. Test papers with p-dimethylaminobenzaldehyde by the Department of Scientific and Industrial Research's method (5) were not satisfactory since the large amounts of hydrogen chloride released iodine from the absorbent in the guard tube and this affected the papers. Some tests were made using phenylhydrazine cinnamate (6). The method was useful for detection but could not be made quantitative. It was then found that the Chemical Defence Research Establishment, Ministry of Supply, had abandoned the sodium thiosulphate/iodide guard tube of the Department of Scientific and Industrial Research's method (5) and replaced it by one containing a mixture of lead acetate and carbonate. This guard tube was found satisfactory, and was also used when estimating phosgene by the standard method of precipitation from aniline hydrochloride.

Results

The effect of temperature on decomposition was measured by burning 0.5 gm samples at different temperatures. The results are given in Table 1 and have been plotted in Fig. 2.

Decomposition commences at low temperatures and is well advanced at 300°C. At this temperature about one third of the chlorine of the original sample is present in the combustion gases. The decomposition becomes rapid at about 600°C. At 1,000°C the chlorine and carbon in the gases correspond to 85 per cent and 90 per cent of the constituents of the original material, indicating that the material is practically completely burned. The effect of ratio of combustible to air was measured by burning 0.25, 0.5 and 1.0 gm (approximately) samples at 550°C and 950°C. The gas analyses are tabulated in Table 2.

With all three ratios of air to plastic the carbon dioxide content of the combustion gases was increased by raising the ignition temperature; and both at 550°C and 950°C was reduced by reducing the air. The carbon monoxide content increased with rising ignition temperature, except for the lowest ratio of air to plastic viz. 1 gm in 5.5 litres, and was lower at 950°C than at 550°C. Varying the ratio of air to plastic produced less change in the content of carbon monoxide than of carbon dioxide. The ratio of carbon monoxide to carbon dioxide was affected by both the temperature and the proportion of combustible to air. The ratio was greater at 550°C than at 950°C, and at each temperature was the same for both the 0.25 gm and 0.5 gm samples. When the sample weight was increased to 1 gm the ratio of the two gases was increased at 550°C but reduced at 950°C. The amount of hydrogen chloride was increased by increasing the ignition temperature, but varying the weight of plastic had only a negligible effect. Phosgene was determined at 350°C and 550°C. In Table 3 the gas concentrations at 350°C and 550°C are compared with recognised safe limits. (7), (8)

The concentrations of phosgene are above the safe, tolerable limit, for prolonged exposure but they are below the one hour limit, whereas the concentrations of the other gases are much greater than those considered dangerous for short exposures; the amount of phosgene produced therefore is relatively insignificant.

Acknowledgements

The gas analyses were made by Mr. P. S. Tonkin.

References

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Table 1

Total chlorine and carbon in combustion gases

Temperature °C	Chlorine		Carbon		Residue % wt.
	As chlorine % wt.	As H.Cl 1/gm	As carbon % wt.	As CO ₂ 1/gm	
295	8.5	0.059	3.1	0.063	49.8
375	8.5	0.059	4.4	0.090	37.3
637	9.9	0.069	7.6	0.155	16.3
768	12.8	0.089	10.9	0.224	10.0
882	18.5	0.128	22.0	0.451	1.6
950	21.9	0.152	35.1	0.719	nil
1,000	22.5	0.156	40.0	0.820	"

Total chlorine in original sample 26.4 per cent.
 " carbon " " " 44.7 per cent.

Table 2

The influence of sample size and ignition temperature on combustion products

Wt. of sample gm.	Temperature °C	Products of combustion (litres of gas/gm material)						
		H.Cl	CO ₂	CO	Ratio CO/CO ₂	COO1 ₂	Hydro- carbon	Hydrogen
0.60	350	0.058	n.d.	n.d.	-	0.00003	n.d.	n.d.
0.280	550	0.071	0.403	0.140	.35	n.d.	0.047	0.040
0.482	"	0.073	0.272	0.092	.36	0.00006	0.263	nil
1.001	"	0.078	0.292	0.185	.74	n.d.	0.090	0.017
0.236	950	0.158	0.742	0.166	.23	n.d.	nil	nil
0.509	"	0.170	0.681	0.162	.24	n.d.	"	0.011
0.917	"	0.169	0.672	0.108	.16	n.d.	"	0.006

n.d. = not determined

Table 3

Concentration of toxic gases

∟Data from Table 2 calculated for a room 10 ft. x 12 ft. 6 in. x 8 ft.
 (1,000 cu. ft.) without ventilations∟

Temperature °C	Weight lb.	Concentration (p.p.m.)			
		Hydrogen chloride	Phosgene	Carbon dioxide	Carbon monoxide
350	6.75	6,300	3.3	n.d.	n.d.
550	5.4	6,300	5.3	23,500	8,000
Safe concentrations for several hours.		10	1.0	5,000(8)	100
Dangerous at 1 hour		50 - 100	25	-	15,00 - 2,000
" short exposure		1,000 - 2,000	50	-	4,000

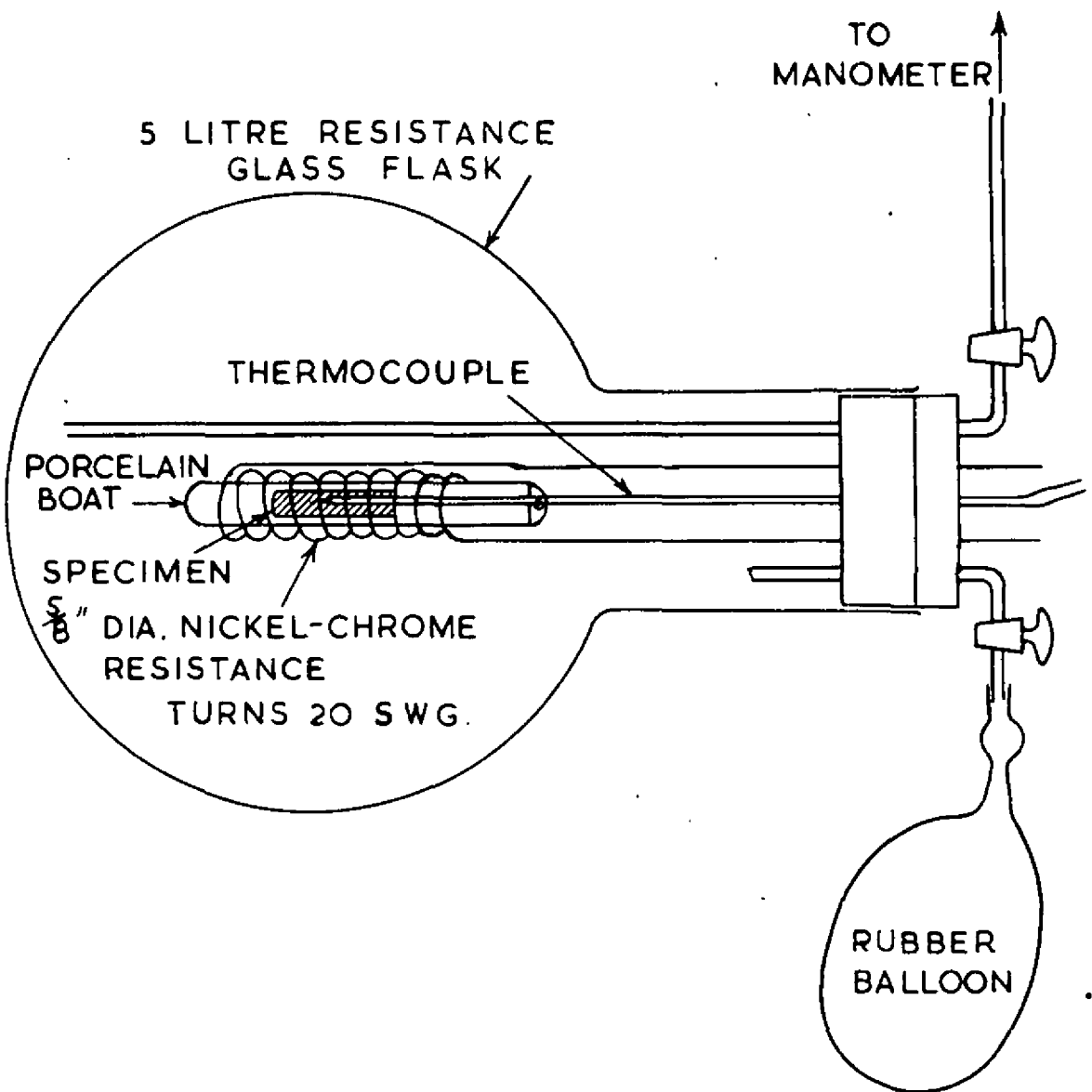


FIG. I. PLAN VIEW OF COMBUSTION CHAMBER.

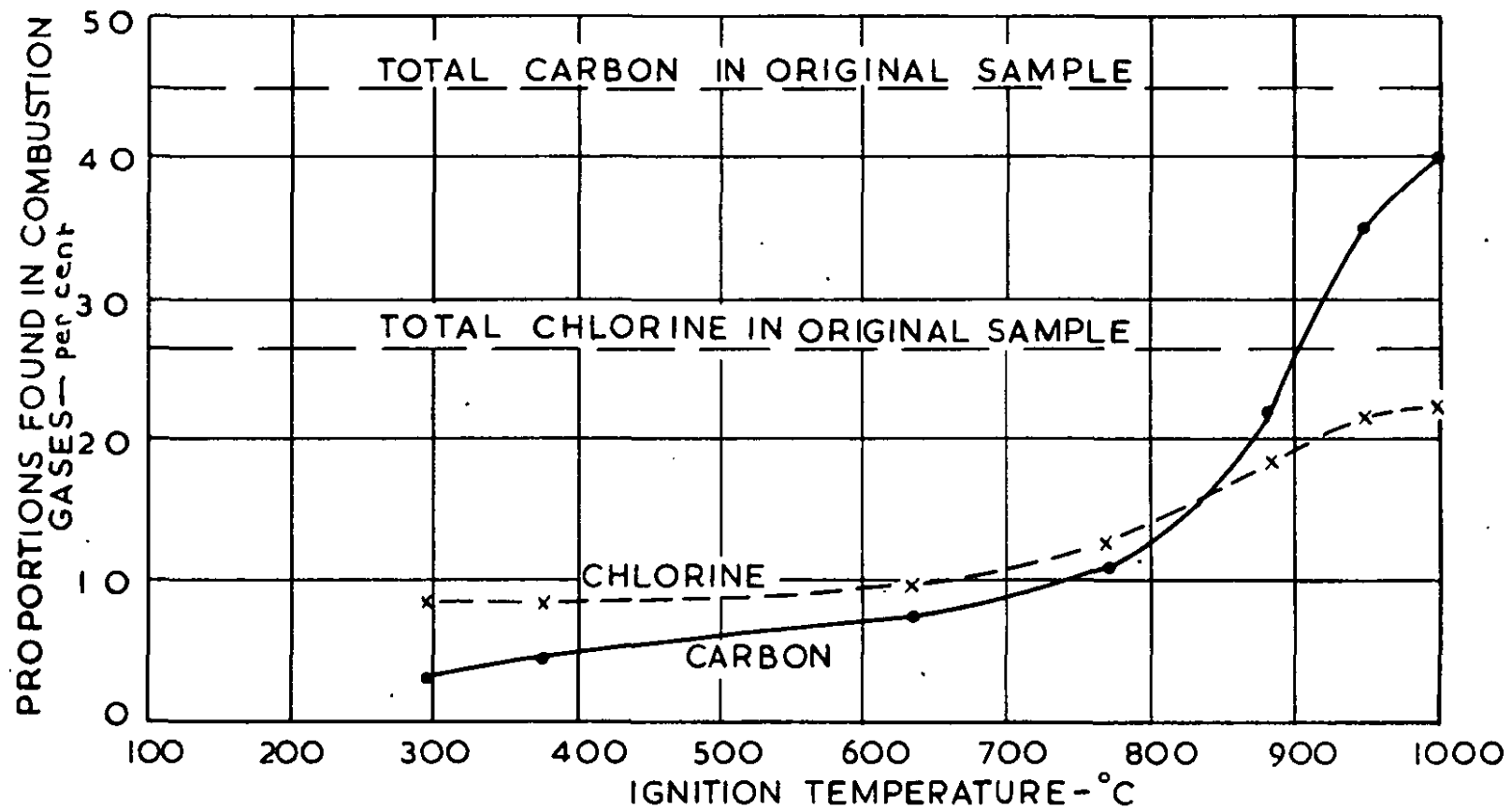


FIG.2. CHLORINE AND CARBON CONTENT OF COMBUSTION GASES.