hexane with n-amyl mercaptan (2. g.mol.) for 40 hours under reflux gave a 23% yield of soluble $Ni(SAm^n)_2$ whilst a 26% yield of insoluble $Ni(SC_6H_5)_2$ was obtained by treatment of a solution of $Ni(SBu^n)$ in cyclohexane with phenyl mercaptan and this demonstrates that mercaptanolysis takes place.

Copper Mercaptides—Cuprous *iso*propylmercaptide (Found: Cu, 46·8; Pr^iS, 53·8. $CuSPr^i$ requires: Cu, 45·9; Pr^iS, 54·1%) and cuprous *n*-amylmercaptide (Found: Cu, 38·2; Am^nS, 61·6 $CuSAm^n$ requires: Cu, 38·1; Am^nS, 61·9%) were precipitated as pale yellow solids by addition of the mercaptan (4 g.mol.) to cupric chloride (1 g.mol.) in 50% aqueous ethanol. They were insoluble in common organic solvents and required treatment with nitric acid or a mixture of hydrochloric acid and hydrogen peroxide to effect solution. They were diamagnetic and thermally stable at 200°/0·1 mm. and are presumably co-ordination polymers.

Zinc Mercaptides—Zinc *iso*propylmercaptide (Found: Zn, 29·0; Pr^iS, 70·2. $Zn(SPr^i)_2$ requires: Zn, 30·3; Pr^iS, 69·7%), zinc *n*-amylmercaptide (Found: Zn, 23·2; Am^nS, 76·1. $Zn(SAm^n)_2$ requires: Zn, 24·0; Am^nS, 76·0%) and zinc phenylmercaptide diammoniate (Found: Zn, 19·6; S, 20·3; C, 46·2; H, 5·0; NH_3, 9·8. $Zn(SC_6H_5)_2,2NH_3$ requires: Zn, 20·6; S, 20·2; C, 45·5; H, 5·05; NH_3, 10·7%) were obtained as white precipitates by the addition of the mercaptan (2 g.mol.) to ammoniacal zinc sulphate (1 g.mol.) solution. The *iso*propylmercaptide and *n*-amylmercaptide were insoluble in common organic solvents but dissolved in pyridine. They were thermally stable at 190°/0·1 mm. and are presumably co-ordination polymers.

It is noteworthy that all of the mercaptides reported in this paper were prepared in the presence of water showing that metal ions with configurations $3d^6$– $3d^{10}$ form hydrolytically stable mercaptides in contrast to the readily hydrolysed mercaptides of titanium (IV).[8]

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The Burning of Polythene

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The burning of polymers, and in particular the prevention of inflammation, is of great practical importance, but very little information is available on the chemistry of the process. We have made, therefore, a study of the burning of polythene from this point of view and the results show features of considerable interest.

The experimental arrangement was essentially very simple. The Grade A polythene was in the form of 1 in. diameter rod, obtained commercially and conforming to BS2919 specification. The material was thus "polyethylene" and this was in accordance with the melting point (110·5°c) and the analysis (27·7 CH_3 groups per 1000 carbon atoms); there were traces of unsaturated groupings, oxygen and a phenolic antioxidant present.* An appropriate length of rod was clamped vertically and a loose-fitting pyrex glass mantle, with a hole approximately 1·5 cm. diameter in the top, placed over the upper end. This end was ignited using a flame from a microburner. The whole was then surrounded by a wide glass tube to act as a draft shield. With a suitable mantle a stable flame was established over the molten polymer (depth about 1–2 cm.), which just did not overflow. Directly above the melt there appeared to be a thin (~1 mm.) non-luminous gap and the flame consisted of a roughly cylindrical blue zone (about 3–4 mm. thick), on top of which was a yellow cone about 3 cm. high.

Temperature profiles were obtained using a thermocouple contained in a thin quartz sheath. Owing to the very high temperature gradient across the liquid surface the temperature values recorded in this region are probably only accurate to 20–30°c. Composition profiles through the flame were obtained by sampling by means of a quartz probe. The samples were analysed by gas-liquid chromatography, except for formaldehyde (chromatropic acid method) and peroxides (ferrous thiocyanate method). A general picture of the results is given in the Table.

The maximum flame temperature is much less than with some other polymers,[1] and, in fact, allowing for the difference in conditions the appearance of the flame and the temperature profile are not dissimilar to those of a three-stage flame of acetaldehyde stabilised in a vertical reactor.[2] Also the flame cannot be considered as a diffusion flame since considerable amounts of nitrogen are present even 1 mm. above the surface of the melt, indicating that air is drawn rapidly in across this surface, although some air probably does diffuse in higher up. Most of the oxygen entering the system just above the surface is consumed very rapidly giving considerably amounts of CO, CO_2 and water. Rough calculations based on the rate of loss of polymer show that the residence time of the material

* We are greatly indebted to Plastics Division, Imperial Chemical Industries Limited for the analysis of a sample.

Table

Temperatures and gas compositions in burning polythene

Position with respect to liquid surface (cm.)	Temp. (°C)	Composition of gas at vertical axis of flame†									
		N_2	O_2	CO	CO_2	H_2O	CH_4	C_2H_4	C_3H_6	$isoC_4H_{10}$	$butenes$
						(mole %)					
1·0 below	180–200										
0·5 below	230–250										
in surface	~400										
0·1 above	~450	75·5	1·1	3·7	10·3	3·7	0·8	1·6	1·3	0·8	1·2
0·4 above	~540	75·6	1·4	3·6	9·6	4·4	0·6	1·5	1·3	0·8	1·2
1·0 above	~640	76·2	1·4	3·5	9·0	5·8	0·5	1·2	1·0	0·7	0·7
2·0 above	~700	77·5	1·5	2·4	9·7	7·9	0·2	0	0·1	0·4	0·3
3·0 above	~650	77·4	1·5	0·2	11·3	9·6	0	0	0	0	0

† The gas composition was the same within experimental error whether probing was from above or from the side of the flame. Traces of C_2H_6, C_3H_8, n-C_4H_{10} and HCHO (<0·1%) were present but no peroxides, ketones or higher aldehydes were detected.

in the mm. above the surface is only a few milliseconds. This is too short at the temperatures involved for degradation products of the polymer leaving the surface to oxidise to the extent found. In fact, the concentration of the hydrocarbons present only decreases appreciably when the temperature has risen well above 600°C. It seems necessary to assume, therefore, that considerably reaction occurs in the surface layer of the melt. This is not unreasonable since liquid phase oxidation at around 400°C would undoubtedly be very rapid, the phenolic additive not acting as an inhibitor at these temperatures.[3]

The combustion process may be tentatively visualised as follows. Heat conduction back from the flame eventually melts the polymer and, as the temperature increases towards the surface of the melt, degradation begins giving lower alkanes and alkenes. In the surface layer rapid oxidation (to give CO, CO_2 and water) and oxidative degradation occur and the products escape, further combustion giving the actual flame. In the blue region relatively slow reaction occurs but as the temperature rises to about 700°C the hydrocarbons are consumed, probably giving mainly "carbon."

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Breakdown of Malathion during Malting Processes

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Malathion (S-[1,2-di(ethoxycarbonyl)ethyl]dimethyl phosphorothiolothionate) is an organo-phosphorus insecticide of low mammalian toxicity which has been accepted by many countries for admixture with raw cereal grains for the prevention of insect infestation. Over the past seven years we have examined several hundreds of samples of home-grown and imported wheat, barley and oats for their malathion content.

A number of maltsters, brewers and distillers have refused to accept barley known to have been treated with malathion. Witt, Case and Adamic[1] have reported that the treatment of barley with malathion has no adverse effect upon the flavour and quality of beers brewed from this barley. Our work has shown

the rapid disappearance of malathion from barley during the process of malting.

We have simulated the malting of barley to which 1·5% malathion dusting powder was added to give a malathion content of 10 p.p.m. and then we determined the malathion content at each stage. We added the malathion powder to twelve 100g. samples of English barley and removed two samples at each stage for extraction and analysis. The method of extraction was by tumbling with carbon tetrachloride and the method of analysis was that described in the *Analyst*.[2]

Recoveries of 85–90% were obtained but the results quoted below have not been corrected for these

Table

Sampling Stage	Added[1]	Found	Added[2]	Found
Barley before steeping	11·6	10·7	10·0	9·0
First steeping liquor removed after 24 hours	10·6	3·0	10·8	3·1
Second steeping liquor removed after second 24 hours	—	1·4	—	1·2
These wet barley samples were inadvertently omitted from analysis				
Barley after 48 hours steeping	10·8	1·2	10·1	1·1
Barley after eight days germination (at lab. temp.)	10·6	0·13	10·5	0·11
Barley after germination and drying at 70°C for seven hours	10·6	0·08	10·8	0·07