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METALLURGY

Spectrographically Pure Metals

Much research work is now being carried out for which metals of the highest degree of purity are desirable. In recent years advertisements or quotations have been received from several sources offering so-called 'pure', 'spectroscopically pure' or 'spectrographically pure' metals, and spectrographic reports have been given suggesting a high degree of purity. Subsequent correspondence has revealed that the reports referred to metallic impurities only, and that non-metals, notably nitrogen, oxygen and carbon, were ignored completely, although some were present to extents far greater than those of the metallic impurities for which the details were given. To those unfamiliar with the subject, a spectrographic report alone may give a quite misleading impression of the purity of a metal, and the importance of obtaining a complete analysis should be emphasized.

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CHEMISTRY

Mechanism of Anti-Knock

There are two theories of the mechanism of anti-knock, one depending on heterogeneous and the other on homogeneous reactions.

The heterogeneous or 'smoke' theory of Muraour[1] is supported by Walsh and his collaborators[2,3], on the basis of their studies of the low temperature oxidation of ethers in coated vessels. The reactions leading to auto-ignitions in the end gas are supposed to be inhibited by removal of chain centres at the surface of the particles.

In view of the very small quantity of lead tetraethyl that is included in gasolines, Egerton[4] postulated that it must act homogeneously. This view has recently received some experimental confirmation from the results of Erhard and Norrish[5], who followed the course of flash-initiated explosions of amyl nitrite, acetylene and oxygen by kinetic spectroscopy. Under these conditions the explosions have the character of homogeneous ignition analogous to detonation and the rate of temperature rise during the induction period is similar to that of the end gas of a spark ignition engine[6]. The inclusion of small partial pressures of lead tetraethyl in the charge increased the induction periods; this is equivalent to the effect of lead in engines, which is to inhibit the pre-flame reactions and to eliminate auto-ignition in the end gas. In these experiments the absorption spectrum of gaseous lead monoxide appeared strongly during the induction periods of one to two milliseconds duration, but there was no evidence for the separation of a solid phase. These experiments were later extended to *n*-heptane and *iso*-octane fuels, in place of acetylene[7], with similar results. Furthermore, it is now known that the maximum end gas temperatures in high compression ratio engines recorded by Livengood, Taylor and Wu[8] are too high to allow of the existence of colloidal lead oxide.

This communication describes in outline results arising from the application of the flash spectroscopic method to a study of the behaviour of some other compounds during explosions of mixtures of amyl nitrite, *n*-heptane and oxygen. The effect of these substances with respect to anti-knock action, smoke formation, effect on induction period (that is, pre-flame reaction) and the emission of light, is indicated by positive and negative signs in the table, which relates to partial pressures of the additives of up to 0·2 mm. A typical charge composition was 3 mm. of amyl nitrite, 2 mm. of *n*-heptane with 40 mm. of oxygen.

Table 1

	Anti-Knock	Smoke	Induction-period	Emission
$TeMe_2$	+	−	+	−
I_2	+	−	+	−
$PbEt_4$	+	−	+	−
$SiMe_4$	−	−	−	−
$SnEt_4$	−	+	−	−
AK-33*X*	+	+	+	+
$Fe(CO)_5$	+	+	−	+
Ferrocene	+	+	−	+
Hg vapour	−	−	−	−
$Hg(iso\text{-}propyl)_2$	−	−	−	−

With the tin and transition metal additives, smokes formed during the induction periods, characterized by a continuous scattering over the entire continuum. *AK*–33*X*[9] (methyl cyclopentadienyl manganese tricarbonyl) under special conditions also acts as a pro-knock by reducing the induction periods. The first three compounds listed in Table 1 all increased the induction periods without smoke formation. Tin tetraethyl gave rise to smoke formation but had no observable effect on the character of the ignition. The formation of colloidal solids has no effect on the auto-ignition delay and there is no correlation with anti-knock action.

A surprising feature of the experiments was that neither ferrocene nor iron pentacarbonyl affected the duration of the induction periods, under a wide variety of fuel compositions and flash energies, in spite of the fact that they are anti-knocks[10,11]. Smokes formed early in the induction periods, probably of colloidal ferric oxide. It is therefore concluded that the iron compounds and colloidal solids, formed during their combustion, do not delay auto-ignition by pre-flame end gas reactions. Since the essential function of any anti-knock is to eliminate