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HEAT RADIATION FROM FIRES OF ORGANIC PEROXIDES AS COMPARED WITH PROPELLANT FIRES

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Summary

This work was carried out to provide information on the safe distance of a store containing organic peroxides from its surroundings. Burning tests were conducted with tertiary butyl perbenzoate (liquid), cyclohexanone peroxide (solid with 10% water), and a nitrocellulose propellant, and radiation intensity measured at various distances. Tests using quantities up to 100 kg indicated the radiation intensity from tertiary butyl perbenzoate to be much greater than from cyclohexanone peroxide, and therefore tests with larger quantities were performed only with the former. It was concluded that 4 kg of organic peroxide gives approximately the same radiation intensity as 1 kg of propellant. The radiation intensity is affected by the diameter of the pool of burning peroxide.

Test set-up

The tests are performed in a fire cage (see Fig. 1) having a surface area of 1.3 × 1.3 m and a height of 2.5 m. The lower part of the cage (until a height of 0.5 m) consisted of a tray to contain the liquid in the cage.

During the tests the radiation intensity was measured at several distances from the fire.

The following radiation meters have been applied:

Radiometer

This radiation meter [1] monitors radiation intensity in that part of the spectrum which is richest in energy (330—2000 nm). With the aid of chromel-constantan thermocouples the temperature rise is measured of a smoke-black golden disc with a thickness of 1.0 mm which is exposed to the radiation. Another disc in the meter which is not exposed to the radiation serves as a reference. The temperature rise is a measure for the quantity of radiation. The average sensitivity is 0.75 $\mu V/(W/m^2)$. In the case of high radiation intensity and/or prolonged radiation time the radiation meter should be cooled with water. As a matter of precaution and also in view of prolonged measurements cooling was practised throughout all the experiments. Maximum measuring range is 4×10^4 W/m^2. Radiation for exposures intensities of less than 1 second are measured too low.

Fig. 1. Fire cage before the test with 25 kg of t-butyl perbenzoate.

Silicon photo diode

This radiation meter monitors radiation intensity in the range 450—950 nm (near infrared visible range). Within this range response is constant. Above 1000 nm and below 400 nm response is smaller than 25 per cent. Linearity covers a range from 10^{-7} to 10 kW/m^2 measuring surface. The upper limit can be extended by means of grey filters.

Of the former type three meters have been applied, positioned at various distances from the radiation source. Of the latter type two meters have been applied, also at various distances from the radiation source.

The calibration of the radiometers is performed in a specially designed, spherical oven. The spherical heating mantle is made of aluminium oxide cement with sodium silicate as a binder.

According to Michaud's formula [2] the emission coefficient of the oven was determined at 0.998. The oven can thus be seen as a black body radiator and according to the law of Stefan—Boltzman ($I = \sigma T^4$, where I = radiation intensity in W/m^2, T = absolute temperature in K, and σ = constant of Stefan—Boltzman = 5.669×10^{-8} W/m^2K) the radiation intensity can be calculated from the oven temperature. The calibration of the radiation meters is carried out at four different oven temperatures.

The calibration of the silicon photo diode was carried out at the proving ground with the help of the radiometers.

The tests were conducted with the following products.

- Cyclohexanone peroxide (a mixture of 1-hydroxy-1'-hydroperoxydicyclohexyl peroxide and bis(1-hydroxycyclohexyl) peroxide) with 10% of water.
- Solid peroxide, packed in cardboard boxes containing 4 plastic bags of 5 kg each.
- t-Butyl perbenzoate, technically pure, liquid peroxide, packed in polythene containers with cardboard outer package, each containing 25 kg.
- Nitro cellulose propellant, web size 0.5 mm, calorific value about 3600 J/g, packed in plastic bags and cardboard outer packages each containing 50 kg (for the tests with 25 kg this package was only half-way filled).

Tests performed and results

The following tests have been performed:

Cyclohexanone peroxide	1 X 20 kg, 2 X 40 kg, 1 X 100 kg
t-Butyl perbenzoate	4 X 25 kg, 2 X 100 kg, 2 X 500 kg
Propellant	4 X 25 kg, 2 X 100 kg, 2 X 450 kg

Figure 2 depicts one of the measuring arrangements applied. Ignition was effectuated by wetting the packing with 1 litre of kerosine and igniting it with the aid of burning wood-wool.

Figures 3, 4 and 5 represent pictures of the nature of the fire-seat for each of the substances under investigation.

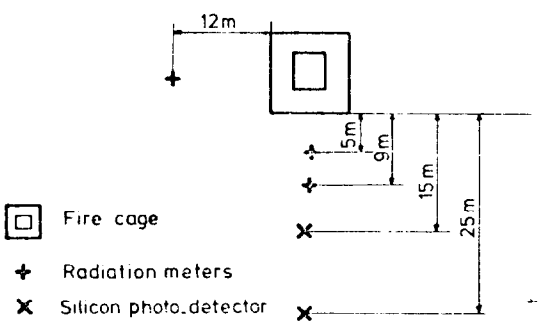

Fig. 2. One of the measuring arrangements used.

Fig. 3. Typical photograph of a fire of 100 kg of cyclohexanone peroxide at its height.

Figure 6 represents the results of the measurements. The mean values of the maximum radiation intensities of tests with identical quantities of substance are plotted in this figure versus the reciprocal of the square of the distance to the radiation source.

Atmospheric disturbances such as for instance wind observed during the measurements have been taken into account when determining the mean values.

The following remarks can be made with respect to these measurements.

(*i*) In many cases it was clearly noticeable when a subsequent package contributed to the fire, for then there was found to be a (temporary) increase in radiation intensity.

(*ii*) In the case of liquid t-butyl perbenzoate the liquid streamed out of the

Fig. 4. Typical photograph of a fire of 500 kg of t-butyl perbenzoate.

package. In the tests with 25 kg and 100 kg this liquid was collected in trays of 0.8 m long × 0.5 m wide × 0.1 m deep and 0.8 m long × 0.8 m wide × 0.1 m deep respectively, and in the test with 500 kg in the tray of the fire-cage (1.3 × 1.3 × 0.5 m). In the test with 25 kg all liquid was contained in the tray, but in the test with 100 kg the capacity of the tray was inadequate, whereas in the test with 500 kg the capacity of the tray was ample but owing to froth formation the peroxide occasionally rose over the rim of the tray.

(*iii*) The duration of the tests and the time during which radiation exceeds 50% of the maximum radiation are listed in Table 1. The increase in the time in the case of t-butyl perbenzoate is not only caused by the increase in quantity but also by the increase in height of the liquid level in the

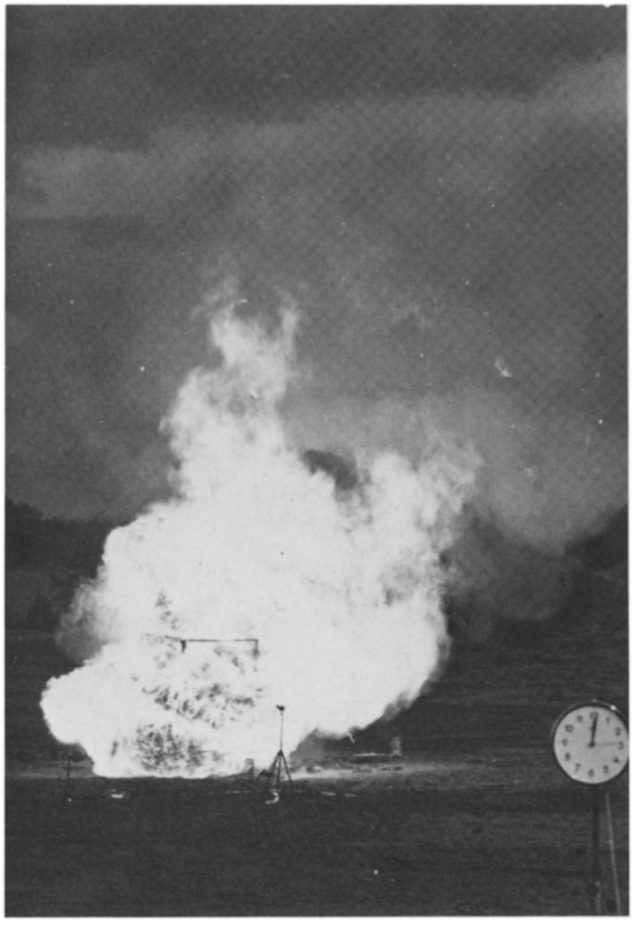

Fig. 5. Typical photograph of a fire of 450 kg of propellant.

tray. Consequently the dimensions of the pool, which determine the thickness of the layer of liquid, are of great importance. The test proceedings have been recorded on film.

(*iv*) For further information the following values are borrowed from literature [3]: The minimum radiation intensity required to ignite wood amounts to 13 kW/m^2, and the radiation intensity which is considered to raise blisters on the human skin amounts to 5 kW/m^2 for thirty seconds.

Conclusions

It proved to be quite feasible to compare the radiation hazard of organic peroxides with that of propellant by means of radiation measurements at

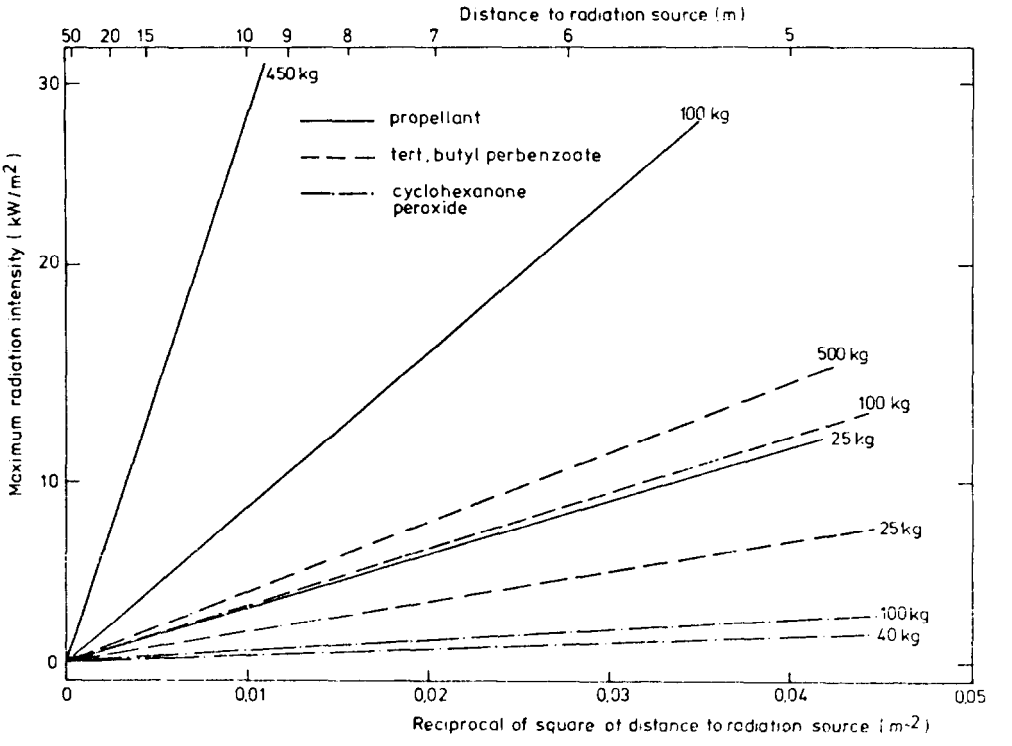

Fig. 6. Maximum radiation intensity as a function of the reciprocal of the square of the distance to the radiation source for the various quantities of organic peroxides and propellant.

TABLE 1

Duration of tests and time during which radiation intensity exceeded 50% of the maximum radiation

Quantity (kg)	Duration of test (sec)			Time (sec) $I > 0.5\ I_{max}$		
	Cyclo-hexanone peroxide	t-Butyl perbenzoate	Propellant	Cyclo-hexanone peroxide	t-Butyl perbenzoate	Propellant
20	600			400		
25		250	60		50	10
40	1000			500		
100	1500	500	80	900	100	30
450			90			70
500		1100			700	

various distances and with different quantities. From Fig. 6 it is apparent that 1 kg of propellant roughly corresponds with 4 kg of organic peroxide from a radiation point of view.

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