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Fire Research Note

No. 677

THE EFFECT OF IMPURITIES ON THE THERMAL
DECOMPOSITION AND EXPLOSION, AND SENSITIVITY,
OF BENZOYL PEROXIDE

by

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November 1967

FIRE
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S U M M A R Y

A limited number of additives have been tested for their effect on the thermal decomposition and explosion, and on the sensitivity to initiation by impact, of benzoyl peroxide. The additives tested were two known decomposition products of the peroxide as well as rust and salts of copper and iron.

The principal effect of the additives is to reduce the induction period for decomposition and explosion. No major effects on the practical hazards of handling and storing the peroxide have been noted.

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MINISTRY OF TECHNOLOGY AND FIRE OFFICES' COMMITTEE
JOINT FIRE RESEARCH ORGANIZATION

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INTRODUCTION

Studies of the isothermal decomposition and thermal explosion of benzoyl peroxide at temperatures below its melting point, which have been reported elsewhere^{1, 2}; were conducted on peroxide samples of commercial purity only (about 98%) because the primary requirement was to determine the behaviour of the material as used in practice.

The present paper reports a limited study of the effect of purification, and of added impurities consisting both of decomposition products and of foreign materials, on the decomposition and explosion. This is necessary for two reasons: first, in so far as impurities may affect the practical explosion hazard as such and, second, because it is well-known that the thermal decomposition of solids can be highly sensitive to factors such as their preparative history and the presence of impurities, and failure to take account of these effects can seriously impair the generality of any conclusions. It is emphasised, however, that only major effects likely to influence the practical hazard significantly are of any interest here.

It has already been shown¹ that the extent to which decomposition products are conserved within the system has a large effect on the induction period for the isothermal decomposition of benzoyl peroxide, while the effect on the maximum rate of decomposition appears to be small.

Initially, in the work reported here, the effect of impurities was studied directly on the thermal explosion of the peroxide. However, owing to the long induction periods for explosion, this direct approach was slow and was therefore supplemented by observations of the isothermal decomposition of the peroxide measured in terms of the evolution of carbon dioxide; this permitted a more rapid examination of a wider range of factors.

The note also includes some observations on the effect of partial decomposition and of the presence of additives on the sensitivity of benzoyl peroxide to initiation by impact.

EXPERIMENTAL

Materials

The benzoyl peroxide used here, and in previously reported work on isothermal decomposition and thermal explosion, was of normal commercial purity, 98-99 per cent, obtained as 3/4 lb "run of the mill" packs from the manufacturer on different dates. The batches will here be designated as follows:-

<u>Batch</u>	<u>Date Obtained</u>
A	March 1961
B	May 1962
C	March 1963
D	December 1963

Part of batch D was purified by recrystallising it once from cold chloroform³ (precipitating with cold methanol), washing with methanol, and drying in vacuo at 40°C.

In addition, an "old" sample of benzoyl peroxide was examined. This was a commercial sample which had been purchased, wetted with water, at the end of August 1957. After eight year's storage in the original bottle, the water had dried out and the peroxide had become yellow in colour and was slightly caked.

The following materials were used as additives:-

1. Natural rust.

This was collected at random by rasping from rusted ironwork in the open air, at the Fire Research Station, Boreham Wood. The rust from all sources was mixed, ground and sieved. Two sieve fractions were used, - 60 B.S. + 120 B.S. and - 240 B.S.

2. Benzoic acid, "Analar" grade.

3. Diphenyl, "laboratory" grade.

4. Copper sulphate pentahydrate, "Analar" grade.

5. Ferrous sulphate heptahydrate, "Analar" grade.

Sample preparation

Only mechanical mixtures of the benzoyl peroxide and additives were examined in this work and, in order to obtain intimate mixing, the materials were ground beforehand. The peroxide was lightly ground by hand, in quantities of about 0.2 g at a time, in an agate mortar behind a toughened-glass safety screen.

For the isothermal decomposition work, in which quantities of about 0.2 g were used, the ground additive and peroxide were mixed in the agate mortar. For the explosion tests, in which quantities of up to 4.6 g were used, the mixing was effected by rotating in a "polythene" container.

A limited assessment of the effect of the grinding and size classification was made on the isothermal decomposition.

Thermal explosion

Minimum temperatures for thermal explosion, and the times to explosion, of the treated benzoyl peroxide were determined for two sizes of charge in the vented furnace as previously described^{2, 4}. As before, the charges were held in open-topped cylindrical containers of aluminium and the depth to diameter ratio was about 1.6.

Isothermal decomposition

In an initial exploration of suitable methods for studying the isothermal decomposition of solid benzoyl peroxide, the commonly used technique of following the evolution of gaseous products in vacuo was found to indicate a course for the decomposition which was different from that found when the decomposition was carried out in air at ordinary pressures and followed in terms of the loss of peroxide. The latter procedure was therefore adopted for the main studies of the isothermal decomposition¹ as being most relevant to the practical problem. However, it eventually became evident that the different behaviour in vacuo probably depended simply on the rapid loss of slightly volatile condensed products important to the decomposition process, and it appeared worthwhile to consider again the possibility of following the decomposition in terms of gas evolution - but in air and at ordinary pressures. This last procedure was adopted for the present work.

A weighed quantity of peroxide (about 0.2 g) was decomposed in a cylindrical glass vessel 14 mm diameter and 15 cm long immersed in a constant temperature oil bath. The reaction vessel was connected by capillary

tubing to a gas burette containing mercury and with provision for telescopic observation. The pressure was adjusted to atmospheric before immersion of the reaction vessel and subsequent readings of gas volume were corrected for the expansion accompanying the immersion. The decomposition was studied at 90°C. (± 0.1 deg C) and, at this temperature, the induction period was such that thermal equilibrium was reached substantially before measurable decomposition occurred.

The fractional decomposition, x , was determined as

$$x = \frac{V_t - V_i}{V_f - V_i} \quad (1)$$

where V_t was the gas volume at time t and V_i and V_f the initial and final volumes, all at N.T.P. Depending on the additives, decomposition was 95% complete within 3 - 8 hours; the final volume was measured at about 20 hours. The total volume of gas evolved was about 15 cm³ at N.T.P. (see further below) and volumes were read to 0.02 cm³.

Sensitivity

The sensitivity to initiation by impact was determined on an impact tester, as used for conventional explosives, using an 8 oz. ball with the sample between $\frac{1}{2}$ " roller bearings.

RESULTS

Thermal explosion

The effect of additives on the thermal explosion of the commercially pure benzoyl peroxide is shown in Tables 1 and 2 for the two sizes of charge examined. The minimum, or critical, explosion temperature has in each case been taken as the mean between the lowest temperature at which explosion occurred and the highest temperature at which no explosion occurred; the induction period given is the value obtained at the lowest explosion temperature

Table 1

Effect of additives on thermal explosion
of benzoyl peroxide
charge diameter 0.86 cm

Additive	Amount per cent	Minimum explosion temperature °C	Induction period min
None	-	90.6 ± 0.2	180
Rust, (- 60 B.S. + B.S.)	1	90.0 ± 0.3	150
Rust, (- 240 BS.)	1	90.7 ± 0.1	90
	2	90.4 ± 0.4	105
Benzoic acid	1	90.4 ± 0.6	130
	2	90.8 ± 0.2	120
	5	89.5 ± 0.1	105
Diphenyl	1	90.5 ± 0.5	130
	2	90.5 ± 0.5	115
	5	90.5 ± 0.4	57

Table 2

Effect of additives on the thermal explosion
of benzoyl peroxide
charge diameter 1.9 cm

Additive	Amount per cent	Minimum explosion temperature °C	Induction period h
None	-	80.6 ± 0.1	33
Rust, (- 240 BS)	1	80.3 ± 0.2	16
	5	79.5 ± 0.3	22
Benzoic acid	1	80.9 ± 0.5	18
	5	80.7 ± 0.7	10
Diphenyl	1	79.9 ± 0.1	20
	5	79.2 ± 0.2	8

The most pronounced effect of the additives tested was reduction of the induction period for thermal explosion. For both sizes of charge, the induction period was most sensitive to the fine rust (- 240 BS), being reduced by about half for an addition of 1 per cent. The decomposition products were almost as effective as the rust in reducing the induction period at the 1 per cent level.

Reductions in the minimum explosion temperature of about 1 deg C occurred following the addition of 5 per cent of benzoic acid to the 0.86 cm charge and 5 per cent rust and diphenyl to the 1.9 cm charge. This effect did not, however, appear to occur consistently. It may be noted also that the minimum temperature for the ground peroxide in the 1.9 cm container was about 1 deg C less than the value reported previously for the unground material (81.4 °C)¹.

Isothermal decomposition

The fractional decomposition, x , defined in equation (1) showed the sigmoid variation with time as previously described¹. The results will here be reported in the form of two derived quantities relevant to the thermal explosion behaviour; these are the maximum rate of decomposition, determined from the maximum slope of the record of x vs. time, and the induction period measured as the time to the maximum rate (time to inflexion). (It has been shown previously² that the induction periods for thermal explosion and isothermal decomposition of benzoyl peroxide are comparable). The variability of replicates was up to about ± 10 per cent of the means for the maximum rates and up to about ± 5 per cent of the means for the induction periods. Except where indicated, all results quoted below are the means of two or more tests and are rounded to the first decimal place.

It is of interest first to compare the results obtained for the isothermal decomposition of benzoyl peroxide in air, measured by gas evolution at ordinary pressures, with the results obtained in terms of peroxide loss and the results for decomposition in vacuo. This comparison is shown in Table 3.

Table 3
Comparison of methods of study of isothermal
decomposition of benzoyl peroxide at 90°C

Experimental Method and conditions	Batch	Maximum rate s ⁻¹ X10 ⁴	Induction period h
Peroxide loss in air	A	1.4	3.9
	D	1.4	4.0
Gas evolution in air	D	1.6	3.8
Gas evolution <u>in vacuo</u> (≤ 10 ⁻² cm Hg)	A	1.2 (± 0.2)	6.6 (± 0.4)

The main effect to be noticed in Table 3 is the increased induction period for decomposition in vacuo. When measured in terms of gas evolution, the maximum rate of decomposition tends to be slightly less in vacuo, and slightly greater at ordinary pressures, than when measured in terms of peroxide loss.

The comparisons in the following tables all refer to measurements of gas evolution accompanying decomposition in air at ordinary pressures.

Table 4 compares peroxide batches, size fractions and the effects of recrystallisation and age.

Table 4
Comparison of batches and treatments

Batch	Treatment	Maximum rate s ⁻¹ X10 ⁴	Induction period h
C	None	1.7	4.7
D	None	1.6	3.8
D	sieved (+ 25 BS)	1.8	3.7
D	ground and sieved (- 60 BS + 100 BS)	1.7	3.8
D	Recrystallised Dried 6 hours <u>in vacuo</u>	1.6	6.3
8 year old sample	None	2.4*	1.8*
" "	Dried <u>in vacuo</u> 4½ hours at 40°C	1.9*	3.0*

* single results

Batches A and B were compared in earlier work¹, and Tables 3 and 4 here complete the comparison of all batches A to D of the benzoyl peroxide used. Apart from the induction period for batch C, which was 20 per cent greater than for the others, there was no significant difference between the batches.

The solid benzoyl peroxide used was a powder containing small agglomerates, and it was noticed that some of the agglomerates in a sample tended to turn yellow at an early stage of the decomposition and in advance of the rest of the sample. However, separate examination of the agglomerates, as the + 25 BS fraction in Table 4, indicated no significant difference in decomposition as measured in terms of the maximum rate and the induction period.

Recrystallisation increased the induction period to a value approaching that observed for decomposition in vacuo, but did not affect the maximum rate of decomposition.

The eight year old sample decomposed more rapidly than usual, the induction period being about half that for the normally available peroxide and the maximum rate 50 per cent greater. The latter result implies that the critical size for thermal explosion of the old sample could be about 25 per cent less, or the critical temperature about 2 deg C less than for the normally available peroxide². This effect was apparently due to the presence of volatile substances since "normal" behaviour tended to be restored after drying in vacuo; this drying resulted also in a weight loss of 1.9 per cent and in reduction of the yellow colour of the "old" material.

The effect of additives on the decomposition of recrystallised benzoyl peroxide, and also the effect of rust on the ground and sieved batch D, is shown in Table 5.

Table 5
Effect of additives on isothermal decomposition
of benzoyl peroxide

Peroxide	Additive per cent	Maximum rate $s^{-1} \times 10^4$	Induction period h
Recrystallised	None	1.6	6.3
	Benzoic acid 1	1.4	3.0
	2	1.4	1.6
	5	1.4	1.2
	Diphenyl 1	1.4	2.1
	2	1.4	1.5
	Rust. -240 BS 2	1.6*	4.2*
	$CuSO_4 \cdot 5H_2O$ 2	1.4*	4.5*
	$FeSO_4 \cdot 7H_2O$ 2	1.5*	4.0*
	Batch D, ground and sieved (-60 BS + 100 BS)	None	1.7
Rust. -240 BS 2		1.9	3.3
5		2.1	3.4

* single results.

As in the earlier thermal explosion results, the principal effect of the additives was reduction of the induction period. The effect was here especially marked for the decomposition products benzoic acid and diphenyl. The addition of decomposition products appeared slightly to decrease the maximum rate of decomposition of the recrystallised benzoyl peroxide. The addition of 5 per cent of rust to the commercially pure peroxide increased the maximum rate of decomposition by 24 per cent. This increase may be expected on theoretical grounds¹ to reduce the critical temperature for thermal explosion by about 1 deg C, and is thus consistent with the reduction noted in Table 2. The effect of rust on the induction period for isothermal decomposition of the material of commercial purity is less than for thermal explosion.

The total amount of gas produced was noted in all cases and was found to be mainly in the range 0.85 ± 0.05 moles of carbon dioxide per mole of benzoyl peroxide. There appeared to be no systematic relationship between the production of carbon dioxide and the treatment of the peroxide or the presence of additives.

Sensitivity

Certain of the additives were tested and found to be without significant effect on the sensitivity of the commercially pure benzoyl peroxide to initiation by impact. Partial decomposition of the peroxide (at 80°C) reduced the sensitivity considerably. These results are shown in Table 6 in terms of the 50 per cent height for initiation by an 8 oz ball.

Table 6
Effect of additives and of partial decomposition
on the sensitivity of benzoyl peroxide to impact

Sample	50 per cent height in
Benzoyl peroxide, commercially pure.	18½
With 2% additive:-	
Rust, (- 60 BS + 120 BS)	17
Rust, (-240 BS)	19
Benzoic acid	21
Diphenyl	17
Partially decomposed:-	
6.4% decomposition	33
66% decomposition	"No go" with 1 lb ball at 72 in

CONCLUSIONS AND COMMENTS

The main effect of the additives tested (consisting of two known decomposition products of the peroxide, rust, and salts of iron and copper), was reduction of the induction period for the decomposition and explosion of benzoyl peroxide. The commercially pure peroxide was most affected in this respect by fine rust (- 240 BS.), the induction period being halved by an addition of 1 per cent. Purification of the peroxide increased the induction period by about 70 per cent., and the purified material was affected most by the addition of decomposition products, benzoic acid and diphenyl.

Reductions of about 1 deg C in the critical temperature for explosions were noted, although not consistently. The maximum rate observed for the isothermal decomposition of an eight year old sample of benzoyl peroxide indicated a possible reduction of about 2 deg C in the critical temperature for explosion, or a 25 per cent reduction in critical size.

The sensitivity of the benzoyl peroxide to initiation by impact was not affected significantly by the additives tested, and partial decomposition reduced the sensitivity markedly.

No effects producing a major increase in the hazards associated with the handling and storage of commercially pure benzoyl peroxide have been noted.

In terms of the model previously adopted for the isothermal decomposition¹, the recrystallised peroxide will have different rate constants for decomposition of the solid phase.

ACKNOWLEDGMENTS

The authors are indebted to Mr. V. J. Clancey, of E2, R.A.R.D.E., for the measurements of impact sensitivity and for advice on their interpretation.

The measurements of isothermal decomposition were carried out by Mrs. M. D. Harris and Mr. P. Field.

The sample of "old" benzoyl peroxide was kindly supplied by Mr. D. Fine of the University of Leeds.

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