

EVALUATION OF THE DEFLAGRATION HAZARDS OF ORGANIC PEROXIDES BY THE REVISED TIME-PRESSURE TEST

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(Received September 29, 1986; accepted January 7, 1987)

Summary

The revised Time-Pressure test has been applied to organic peroxides to evaluate their deflagration hazards. Liquid organic peroxides were also tested successfully using a firing method with a fusehead. The results show that the ignition sensitivity and the violence of deflagration can be obtained from the amount of igniting material giving the apparent maximum rate of pressure rise, and its maximum rate, respectively. From an evaluation of the deflagration hazards of many types of organic peroxides, it is also shown that the ignition sensitivity and the violence of deflagration for each organic peroxide may have a tendency to increase with increasing active oxygen content among the same type of organic peroxide, with a few exceptions and that the ignition sensitivity and the violence of deflagration for each type of organic peroxide may decrease in the following order, given the same active oxygen content: diacyl peroxides > peroxyesters > dialkyl peroxides > hydroperoxides.

1. Introduction

The Time-Pressure test was originally designed at RARDE (Royal Armament Research and Development Establishment, U.K.) and was developed at

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HSE (Health and Safety Executive, U.K.) as a test to examine the effects of ignition on hazardous materials under confinement and, in particular, the possibility that ignition might lead to deflagration with explosive violence at pressures which could be attained with materials in normal commercial packages [1,2].

The authors have attempted to apply the revised Time-Pressure test [3] to various hazardous materials, such as blowing agents, mixtures of an oxidizer and a combustible [4-6], and explosives diluted with an inert filler [7], to evaluate their deflagration hazards. The results show that the revised Time-Pressure test can be useful for obtaining information on the deflagration hazards of unstable materials.

In this work we have attempted to apply the revised Time-Pressure test to organic peroxides. The testing procedure for liquid samples has been examined to evaluate the deflagration hazards of liquid organic peroxides. In addition, the effects of the amount of an igniting material on the rate of pressure rise, due to the ignition of an organic peroxide, have also been examined. This paper describes the testing procedure for liquid organic peroxides, the effects of the amount of the igniting material on the rate of pressure rise, and some findings on the ignition sensitivity and the violence of deflagration for various types of organic peroxides.

2. Experimental

2.1. Materials

Organic peroxides were supplied from Nippon Oil & Fats Co., Ltd., and used as samples for the revised Time-Pressure test without further purification. The properties of the organic peroxides are shown in Table 1.

An igniting material was prepared by carefully mixing Pb_3O_4 (70 wt%) and Si (30 wt%) with a brush. Pb_3O_4 and Si were of reagent grade and purchased from Wako Chemical Co., Ltd.

2.2. Apparatus

The Time-Pressure test originally designed at RARDE, U.K. [1,2], was partially revised [3]. Figure 1 shows a cross-section of the revised Time-Pressure test apparatus. The apparatus consist of a cylindrical closed vessel made of steel (25 mm internal diameter, 55 mm long, ca. 27 cm³ capacity), fitted with an ignition device and connected to a pressure recording system. Both ends of the cylinder are bored and threaded to accept steel closure plugs. One plug is fitted with electrodes to which a nichrome wire heater (0.05 mm outer diameter, 100 mm long) or a fusehead is attached to fire an igniting material by an exploder (12 V). The other plug serves to retain a rupture disc made of brass (25 mm diameter, 0.15 mm in thickness) which vents to the atmosphere at a pressure of about 1500 psi (100 N/cm²) to protect the appa-

TABLE 1

Deflagration properties of organic peroxides

Sample, 5 g; igniter, Pb₃O₄ (70 wt%) - Si (30 wt%); firing method, firing with a nichrome wire or a fusehead; rupture disc, brass, 0.15 mm in thickness.

Organic peroxide	Purity (wt.%)	Active oxygen ^a (wt.%)	Physical appearance	Deflagration properties		
				Amount of igniter ^b (g)	Δtime (ms)	
					100-300 (psi)	300-500 (psi)
<i>1. Dialkyl peroxides</i>						
Di-t-butyl peroxide	99.0	10.83	liquid	3	140	32
t-Butyl cumyl peroxide	90.1	6.92	liquid	5	no pressure rise	
Dicumyl peroxide	98.0	5.80	flake	5	no pressure rise	
α,α'-Bis(t-butylperoxy)- diisopropylbenzene	99.0	9.38	flake	1	160	70
2,5-Dimethyl-2,5-di-(t- butylperoxy) hexane	90.1	9.93	liquid	5	no pressure rise	
2,5-Dimethyl-2,5-di-(t- butylperoxy) hexyne-3	93.8	10.48	liquid	1	56	13
<i>2. Diacyl peroxides</i>						
Decanoyl peroxide	98.0	4.58	powder	5	no pressure rise	
Lauroyl peroxide	99.3	3.98	flake	5	no pressure rise	
Benzoyl peroxide	99.9	6.61	powder	1	0.33	0.15
3,5,5-Trimethyl-hexanoyl peroxide	75.0	3.82	liquid	5	no pressure rise	
<i>3. Hydroperoxides</i>						
t-Butyl hydroperoxide	80.6	14.31	liquid	1	160	54
Cumene hydroperoxide	82.0	8.62	liquid (in hydrocarbon)	5	no pressure rise	
Diisopropylbenzene hydroperoxide	54.0	4.45	liquid (in hydrocarbon)	5	no pressure rise	
p-Menthane hydroperoxide	52.7	4.90	liquid (in hydrocarbon)	5	no pressure rise	
2,5-Dimethylhexane 2,5- dihydroperoxide	79.6	14.29	powder (20wt%:H ₂ O)	1	82	30
<i>4. Peroxyesters</i>						
t-Butyl peroxybenzoate	99.0	8.16	liquid	1	120	13
Di-t-butyl diperoxy- isophthalate	82.0	8.45	powder (20wt%:H ₂ O)	1	4.4	1.3
2,5-Dimethyl-2,5-di (benzoylperoxy) hexane	97.0	8.03	powder	1	13	4.9
t-Butyl peroxy maleic acid	98.8	8.40	powder	1	5.9	1.9
t-Butyl peroxyiso- propylcarbonate	98.0	8.90	liquid	4	230	37
t-Butyl peroxy laurate	99.1	5.82	liquid	5	no pressure rise	
t-Butyl peroxy pivalate	70.0	6.43	liquid	5	no pressure rise	
<i>5. Others</i>						
1,1-Bis(t-butylperoxy)- 3,3,5-trimethylcyclohexane	90.1	9.54	liquid	1	50	21
n-Butyl 4,4-bis-(t- butylperoxy) valerate	88.2	8.44	liquid	2	120	36
Methyl ethyl ketone peroxide	56.6	10.30	liquid	1	97	42

^aActive oxygen (wt%) = $\frac{(\text{atomic weight of oxygen}) \times (\text{number of } -\text{O}-\text{O}- \text{ bond})}{(\text{molecular weight})} \times \text{purity (wt\%)}$.

^bAmount of igniter giving the apparent maximum rate of pressure rise.

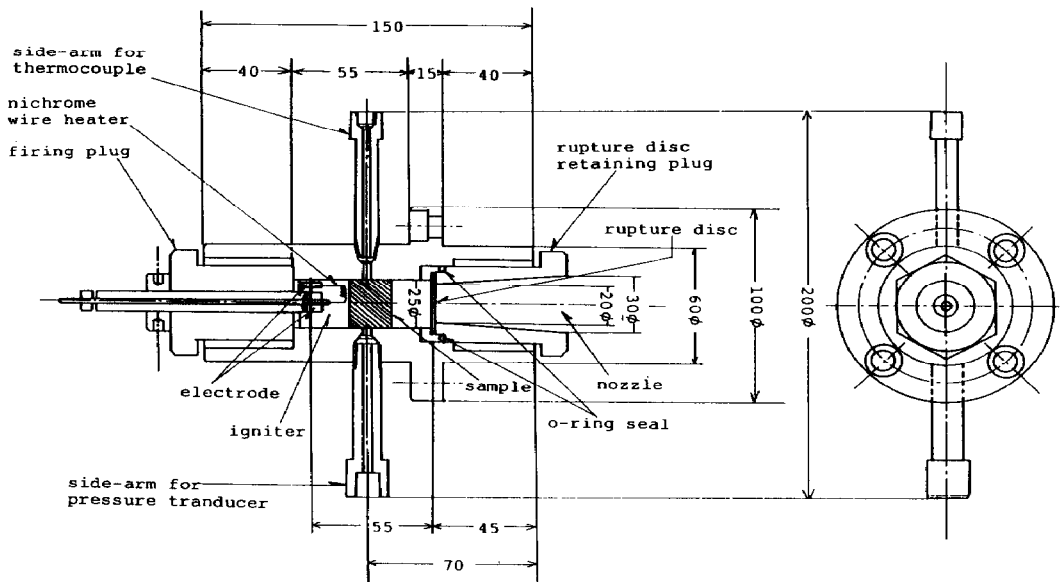


Fig. 1. Cross-section of the revised Time-Pressure test apparatus.

ratus from generating excessive pressure. The pressure developed in the chamber is detected with a pressure transducer (Type 6211 from Kistler Co., Ltd.) in the tubular side-arm (4 mm internal diameter, 85 mm long), amplified with a charge amplifier (Type 5001 from Kistler Co., Ltd.) and recorded with a digital memory scope (Type 4562/4094 from Nicolet Co., Ltd.).

2.3. Test procedure

A nichrome wire heater is used to fire the igniting material; 1–5 g of the igniting material is introduced into the chamber so as to be in sufficient contact with the nichrome wire heater and then 5 g of a solid sample is placed on it.

When a fusehead is used to fire the igniting material, 1–5 g of the igniting material, including the fusehead placed in its center, is wrapped with a polyvinylidene film from Asahi Chemical Co., Ltd. (10 mm × 10 mm, 10 μ m in thickness), and the igniting material is placed in the center of 5 g of a sample and the sample is wrapped again with the film. Figure 2 shows the firing system with a fusehead for liquid samples. In some experiments to examine the effects on the time–pressure profile of the difference in the firing system between the nichrome wire method and the fusehead method by using solid samples, the firing system with a fusehead is also applied to solid samples. Thus, the fusehead of the sample prepared is fixed to the electrodes on the plug.

After the sample is introduced into the chamber, a rupture disc is placed in

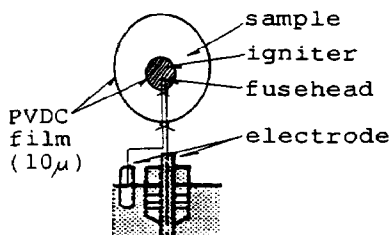


Fig. 2. Firing method with a fusehead for a liquid sample.

position and the rupture disc retaining plug is screwed into place and tightened with a wrench.

The rupture disc retaining plug is then connected to a muffler to weaken the explosion sound and the firing leads are connected to the terminal of the electrodes on the plug to which the igniting system is fixed.

A charge is then ignited by operating the dynamo at a remote place.

The time intervals for the pressure to rise from 100 to 300 psi (from 7 to 21 N/cm²) and from 300 to 500 psi (from 21 to 35 N/cm²), due to the deflagration of an organic peroxide in the chamber, are measured to evaluate its deflagration hazards.

3. Results and discussion

3.1. Firing with a fusehead

The effects on the time–pressure profile of the difference in the firing system between the nichrome wire method and the fusehead method, especially for liquid samples, have been examined by using some solid samples.

It can be considered that there might be two major effects on the time–pressure profile of the difference in the firing system for both solid and liquid samples: (1) the difference in the firing system might not have direct effects on the profile but have indirect effects on the profile as the results of its direct effects on the combustion behaviour of the igniter; and (2) the combustion of the polyvinylidene film, a wrapping material, might also have some effects on the profile.

As shown in Table 2, there is no remarkable difference in deflagration properties due to the firing method. Therefore, it may be said that the firing method with a fusehead can be applied to liquid samples.

3.2. Ignition sensitivity and violence of deflagration

In order to attempt to apply the revised Time–Pressure test to organic peroxides which have a different ignition sensitivity, the apparent rates of pressure rise ($1/\Delta t$) have been measured by using 1 to 5 g of the igniting material. Δt is the time interval required for the pressure to rise from 100 to 300 psi

TABLE 2

Effects of firing methods on the deflagration properties of organic peroxides by the revised time-pressure test

Sample, 5 g; Igniter, Pb_3O_4 (70wt%) - Si (30wt%); Firing method, Nichrome: firing with the nichrome wire from the lower side, Priming: firing with the fusehead in the center of the samples; Rupture disc, brass, 0.15 mm in thickness.

Organic peroxide (active oxygen (wt%))	Firing method	Igniter			
		1 g		3 g	
		Δ time (ms)		Δ time (ms)	
		100-300 psi	300-500 psi	100-300 psi	300-500 psi
Benzoyl peroxide (6.61)	Nichrome	3.3×10^{-1}	1.5×10^{-1}	4.2×10^{-1}	1.4×10^{-1}
	Priming	4.0×10^{-1}	1.9×10^{-1}	3.6×10^{-1}	1.4×10^{-1}
2,5-Dimethyl- 2,5- di(benzoylperoxy) hexane (8.03)	Nichrome	1.3×10	5.6	1.2×10	4.8
	Priming	1.4×10	4.4	1.3×10	4.7
2,5-Dimethylhexane 2,5- dihydroperoxide (14.29)	Nichrome	5.8×10	3.1×10	6.7×10	3.2×10
	Priming	1.0×10^2	2.1×10	1.2×10^2	3.1×10

or from 300 to 500 psi due to the deflagration of an organic peroxide. Figure 3 shows changes in the apparent rates of pressure rise for different amounts of the igniting material in the deflagration of some organic peroxides. Some organic peroxides, such as benzoyl peroxide and α, α' -bis (t-butylperoxy) -diisopropylbenzene which have a high ignition sensitivity, show their apparent maximum rates of pressure rise with even 1 g of the igniting material; while some organic peroxides, such as dicumyl peroxide, t-butyl peroxy laurate and cumene hydroperoxide which have a low ignition sensitivity, do not show a detectable pressure rise with even 5 g of the igniting material. However, such organic peroxides as n-butyl 4,4-bis (t-butylperoxy) valerate, di-t-butyl peroxide and t-butyl isopropylperoxycarbonate which have an intermediate ignition sensitivity, do not show a detectable pressure rise with 1 g of the igniting material but do show their apparent maximum rates of pressure rise with a larger amount of igniting material. Therefore, the ignition sensitivity of an organic peroxide may be obtained from the amount of the igniting material giving the maximum rate of pressure rise.

On the other hand, benzoyl peroxide shows a remarkably high apparent maximum rate of pressure rise, but t-butyl isopropylperoxycarbonate shows an apparent lower maximum rate. Thus some knowledge of the violence of deflagration may be obtained from the apparent maximum rate of pressure rise.

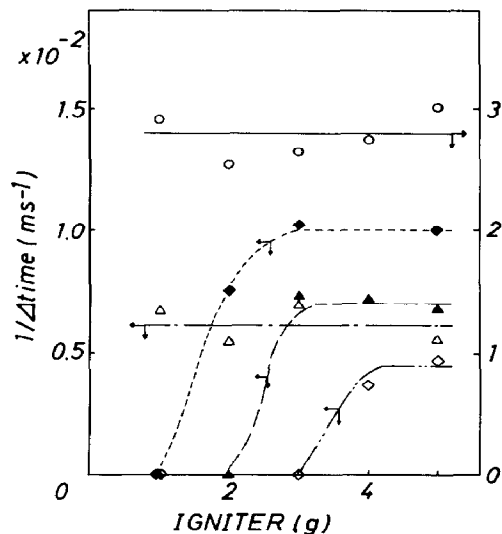


Fig. 3. Changes of $1/\Delta\text{time}$ with the amount of the igniter in the deflagration of some organic peroxides. Key: ○, benzoyl peroxide; △, α,α' -bis(t-butylperoxy-*p*-isopropyl)benzene; ▲, di-*t*-butyl peroxide; ◇, *t*-butyl peroxyisopropylcarbonate; ◆, *n*-butyl 4,4-bis(t-butylperoxy)valerate.

3.3. Evaluation of the deflagration hazards of organic peroxides

The deflagration hazards of various organic peroxides have been examined by using different amounts of the igniting material in the revised Time-Pressure test. Table 1 shows the ignition sensitivity obtained from the amount of igniting material giving the apparent maximum rate of pressure rise, and the violence of deflagration obtained from its time intervals for the pressure rise from 100 to 300 psi and from 300 to 500 psi. Figures 4 and 5 show changes in the amount of igniting material giving the apparent maximum rate of pressure rise, and its maximum rate for a given content of active oxygen, respectively, for each group of organic peroxides which has the same type of peroxy group. To show widely different rates data in one figure, the apparent rates of pressure rise are expressed in terms of $-\log(\Delta\text{time})$ in Fig. 5. Therefore, several data indicating zero apparent rate cannot be shown in Fig. 5 because their values of $-\log(\Delta\text{time})$ are $-\infty$.

According to a proposal on the criteria of a deflagration hazard with the Time-Pressure test to the International Group of Experts on the Explosion Risks of Unstable Substances, Organization Committee for Economic Co-operation and Development (OECD-IGUS) by Mr. Turner at HSE, U.K., a substance is considered to present the hazard of explosion by deflagration if the time interval for a pressure rise from 100 to 300 psi is less than 30 ms [2]. From this criteria it may be said that benzoyl peroxide (diacyl peroxide), di-*t*-butyl diperoxyisophthalate, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane and *t*-butyl peroxy maleic acid (peroxyester) are shown to have hazards of explosion by deflagration.

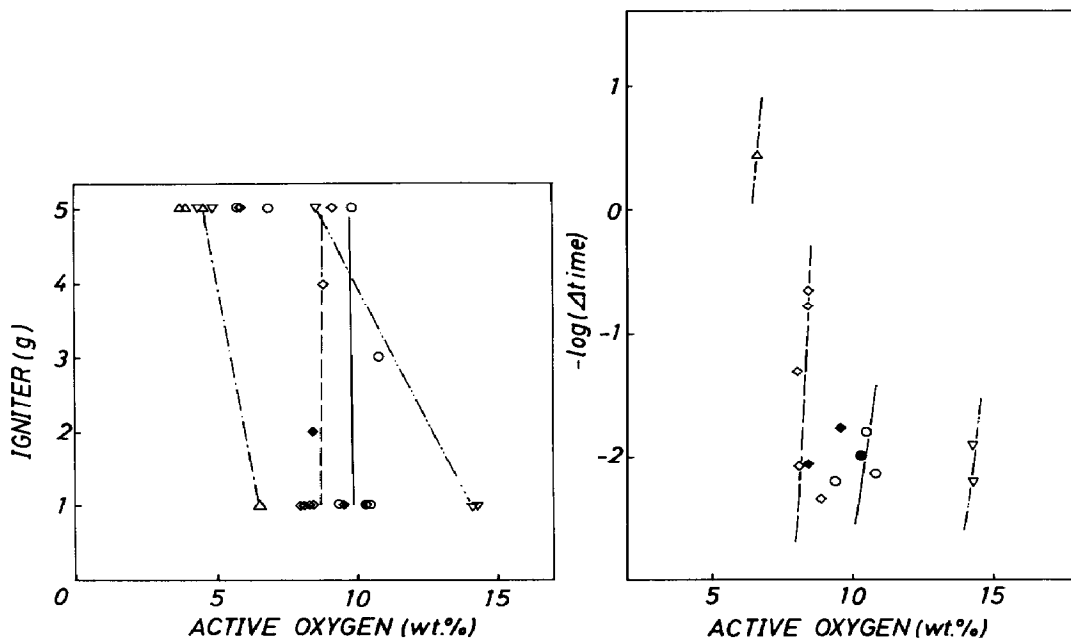


Fig. 4. Changes of the amount of the igniter giving the apparent maximum rate of pressure rise with a content of active oxygen in the deflagration of organic peroxides. Key: \circ , dialkyl peroxide; Δ , diacyl peroxide; \diamond , peroxyester; \blacklozenge , peroxyketal; ∇ , hydroperoxide; \bullet , ketone peroxide.

Fig. 5. Changes of $-\log(\Delta t/ime)$ with a content of active oxygen in the deflagration of organic peroxides. Key: \circ , dialkyl peroxide; Δ , diacyl peroxide; \diamond , peroxyester; \blacklozenge , peroxyketal; ∇ , hydroperoxide; \bullet , ketone peroxide.

From the data, organic peroxides having a higher content of active oxygen may have a higher ignition sensitivity and a higher violence of deflagration among each group of organic peroxides. In addition, both the ignition sensitivity and the violence of deflagration at the same content of active oxygen seem to become lower in the following order:

diacyl peroxide > peroxyester > dialkyl peroxide > hydroperoxide

3.4. Comparison of the rates of pressure rise with PVLD values

The pressure vessel test is known to give some information on the violence of thermal decomposition on heating [8–11]. The apparent rates of pressure rise, which show the violence of deflagration on igniting, are compared with their corresponding limiting nozzle diameters in the pressure vessel test (PVLD) [11], which show the violence of thermal decomposition on heating.

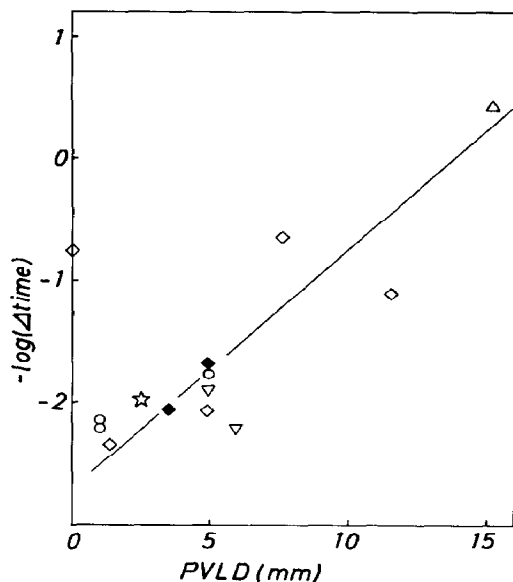


Fig. 6. Comparison of $-\log(\Delta\text{time})$ in the T-P test with the PVLD value in the pressure vessel test for organic peroxides. Key: ○, dialkyl peroxide; △, diacyl peroxide; ◇, peroxyester; ◆, peroxyketal; ▽, hydroperoxide; ☆, ketone peroxide.

Figure 6 shows the relationship between both data. Although the stimulus energy which initiates a deflagration or decomposition is different in both test methods, it may be said that organic peroxides which have higher apparent rates of pressure rise should have higher PVLD values among the organic peroxides tested.

4. Conclusions

The revised Time-Pressure test has been applied to organic peroxides to evaluate their deflagration hazards. Liquid organic peroxides could also be tested successfully by using the firing method with a fusehead.

The results show that the ignition sensitivity and the violence of deflagration can be obtained from the amount of igniting material giving the apparent maximum rate of pressure rise and its maximum rate, respectively. The data also show that the ignition sensitivity and the violence of deflagration of an organic peroxide may have a tendency to increase with increasing active oxygen content among the same group of organic peroxides, with a few exceptions and that the ignition sensitivity and the violence of deflagration of each group of organic peroxides may decrease in the following order, given the same active oxygen content:

diacyl peroxide > peroxyester > dialkyl peroxide > hydroperoxide

In addition, the apparent rates of pressure rise giving the violence of deflagration in the revised Time-Pressure test seem to be correlated with the PVLVD values giving the violence of thermal decomposition among organic peroxides tested, although the stimulus energy to initiate a deflagration is different from that to initiate a thermal decomposition.

Acknowledgements

The authors wish to thank The Industrial Explosives Society, Japan, and Professor Iwama at The Institute of Space and Astronautical Science for their financial support. The authors also wish to thank Nippon Oil & Fats Co., Ltd. for the kind gifts of the organic peroxides.

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