HAZARD EVALUATION OF ORGANIC PEROXIDES

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Summary

A comprehensive study on the hazard characteristics of organic peroxides was made with a view towards identifying the type of tests that might be useful in arriving at a hazard classification scheme. This included (a) detonability tests, (b) thermal stability—explosion tests, and (c) energy release tests. The following peroxides were investigated in this study: Benzoyl peroxide (BP), dicumyl peroxide (DCP), diisopropyl peroxydicarbonate (IPP), tertiary-butyl perbenzoate (BPB), methyl ethyl ketone peroxide/dimethyl phthalate (MEKP) (9% and 11% active oxygen), and hydrogen peroxide (HP).

Results obtained from the various tests performed indicate that these tests clearly delineate the relative hazards of the peroxides investigated. It appears that the organic peroxides can be tentatively classified into three categories: (1) Compounds that may pose a detonation hazard, e.g., IPP, which undergoes an unsteady low-velocity detonation, (2) compounds that exhibit potential deflagration properties, e.g., BP, MEKP (9% and 11% active oxygen) and BPB, and (3) compounds that may possess only fire hazard potential, e.g., DCP. Attempts to correlate the various experimental test results with the physicochemical properties of the peroxides, such as oxygen balance, active oxygen content, maximum heat of decomposition, difference between heat of combustion and heat of decomposition, and gas volume, met with moderate success and shed some light on the role of the various cited properties in determining the sensitivity and stength of the peroxides.

Introduction

Organic peroxides constitute a class of chemicals that exhibit unique hazard characteristics. They may, or may not, simultaneously exhibit thermal instability and sensitivity to shock, impact, and/or friction, and they may be flammable [1—4]. An understanding of the potential hazards of peroxides is imperative for their safe manufacture, handling, and usage. Any attempt to do this is beset with difficulties because the characteristics cited, as well as their interdependence, need to be evaluated before hazards can be assessed. A few previous studies [1—4] were undertaken along these lines; however, no definite correlations were found between the hazard potential of the peroxide and the concentration, active oxygen content, or the type of peroxide under investigation. Special consideration must also be given to factors such as storage or packaging conditions for each compound.

Several researchers have attempted to evaluate the hazard characteristics of organic peroxides and arrive at a hazard classification system for commercial products [1,5,6]. Most of these studies met with considerable success and resulted in a relative hazard classification system. The principal tests previously used for hazard evaluation include the following:

1. 50/70 tube test to determine detonability.
2. Thermal explosion tests in polyethylene or aluminum containers.
3. Pressure vessel test.
4. Lead pipe deformation test.
5. Self-accelerating decomposition test.
6. Flash point test for liquid peroxides.
7. Impact and friction sensitivity tests.

The first two tests were recommended by the Technological Laboratory, TNO, Rijswijk (Netherlands) [5,6], while the others were adopted by Noller et al. [1] in their hazard classification scheme. A special merit of the tests developed by the Technological Laboratory is that notice is taken of the fact that the nature of packaging affects the sensitivity of the peroxides; thus, these test results provide a criterion for their classification for transportation purposes. These two investigations have been the most comprehensive studies carried out thus far on peroxides.

The present work was carried out with the following objectives:

1. To investigate the shock sensitivity, thermal stability-explosion risk, and energy release properties.
2. To identify, if possible, the type of tests to be carried out that are pertinent to the construction of a hazard classification system.
3. To estimate the TNT equivalence for commercial organic peroxides and to assess the significance of the values so generated.

The organic peroxides chosen in the present study were benzoyl peroxide (BP), tertiary butyl perbenzoate (BPB), dicumyl peroxide (DCP), diisopropyl peroxydicarbonate (IPP), and methyl ethyl ketone peroxide/dimethyl phthalate (MEKP). In addition an inorganic peroxide, hydrogen peroxide (HP), was included.

Table 1 gives the name of the supplier, concentration or percent active oxygen, and physical state of the peroxides investigated in the present study.

The tests carried out in the present study can essentially be categorized into three classes:

Class A: Detonability tests
        A1. Card-gap test (Shock sensitivity test).
        A2. Deflagration-to-detonation transition test (DDT test).
Class B: Thermal stability-explosion tests
        B1. Koenen and Ide B.A.M. test.
        B2. Thermal explosion test.
Class C: Energy release tests
        C1. Heavy confinement cap test.
        C2. Ballistic mortar test.
        C3. Underwater test method.

TABLE I

Tabulation of peroxides investigated

Sample	Manufacturer	Concentration (%)/ % active oxygen (AO)	Physical state
Benzoyl peroxide (BP)	Aztec Chemical, Ohio	98	Solid
Dicumyl peroxide (DCP)	Hercules Inc., Delaware	100	Solid
Diisopropyl peroxydicarbonate (IPP)	PPG Industries Inc., Pittsburgh	100	Solid
t-Butyl perbenzoate (BPB)	Lucidol, Pennwalt, New York	100	Liquid
Methyl ethyl ketone peroxide/di-methyl phthalate (MEKP)	Noury Chemical Corp., New York	11% AO	Liquid
Methyl ethyl ketone peroxide/ dimethyl phthalate (MEKP)	Noury Chemical Corp., New York	9% AO	Liquid
Hydrogen peroxide (HP)	FMC Corp., New Jersey	70	Liquid

The tests were selected to make the present study reasonably comprehensive and to obtain an overview of the potential hazards of the peroxides. Thus, the tests in Class A determine whether the substance will detonate or exhibit explosive properties when subjected to a strong shock or thermal stimulus. The tests included in Class B provide information regarding the thermal stability of the peroxides — the rate and/or violence associated with their thermal decomposition as well as their susceptibility to autoignition. The aim was to ascertain whether or not the tests cited could differentiate hazards among the various peroxides and/or provide a useful hazard rating for them. The energy release tests (Class C) offer a method for estimating the TNT equivalence, a quantity that might be useful in determining an index for their damage potential. It appears that such an attempt has not been made to date. However, it should be pointed out that the significance of the TNT equivalence values calculated from the above tests must be properly interpreted for practical application.

In addition to the above experimental tests, the ASTM CHETAH computer program (CHEmical Thermodynamic And Hazard analysis program) was used to obtain additional information regarding the hazard ratings for the various peroxides [8]. The values obtained for the various criteria in the CHETAH program were used to seek correlations between the experimental test results and CHETAH criteria. The CHETAH criteria were (1) the maximum heat of decomposition (ΔH_d), (2) the difference between heat of combustion and heat of decomposition ($\Delta H_c - \Delta H_d$), and (3) the oxygen balance (OB). A

fourth variable (gas volume) (GV), calculated from the decomposition products predicted by CHETAH program, was also used. The test results are those from the (1) heavy confinement cap test, (2) ballistic mortar test, and (3) underwater test. It should be mentioned here that attempts to correlate the experimental results with the CHETAH criteria may have limited value in view of the fact that the values obtained from the various criteria using the CHETAH program are for reactions under "ideal" conditions (maximum enthalpy of decomposition where the available oxygen first oxidizes hydrogen to water and then carbon to carbon dioxide). Furthermore, no attempt has been made to include the reaction kinetics in this study, but it was believed that such an analysis could provide some insight into the role played by each of the above-mentioned parameters in the different experimental tests. A standard multiple linear regression technique was used in the correlation studies.

Experimental procedures

Class A: Detonability tests

A1. Card-gap test
The procedure outlined by Hay and Watson [9] for defining explosive substances has been adopted in the study. The test sample was contained in a 40 cm long, cold-drawn seamless mechanical tube, having a 4.76 cm outside diameter and a wall thickness of 0.55 cm. A cast pentolite booster, 5.00 cm in diameter and 5.00 cm long, weighing about 175 g was used to initiate the test charge. In some tests, a cast acrylic plastic cylinder (Plexiglas) was used to attenuate the shock wave. The plastic cylinder was also 5.00 cm in diameter, and its length could be varied to change the shock amplitude. Two techniques were used to determine whether the test sample had detonated. In one, a 0.317 cm thick by 15 cm square mild steel witness plate positioned 0.159 cm (standoff) beyond the downstream end of the test charge was used; a hole in the plate confirmed the occurrence of a detonation. In the other technique, a continuous-velocity probe was employed to measure the detonation velocity. The fragmentation pattern of the steel tube, the witness plate damage, and the amount of sample consumed were also used to aid in the evaluation. Except where noted, all tests were carried out at $20° ± 1°C$.

A2. Deflagaration-to-detonation transition test
This test was also carried out as per the recommendations of Hay and Watson [10]. The test material was loaded into a non-vented bomb which consisted of a 45.7 cm long, schedule 80 steel pipe having an inside diameter of 7.37 cm and a wall thickness of 0.76 cm. The pipe was capped at both ends with forged steel pipe caps. The igniter employed in the current work consists of 20 g of 50/50 RDX and FFF_g black powder mixture contained in a tube formed from 0.025 cm thick cellulose acetate sheet, reinforced with a double layer of nylon-filament-reinforced tape. The igniter, positioned

internally at the center of the test material, is initiated by a 1 cm length of B&S No. 28 gage (0.032 cm diameter) Nichrome* wire heated by a current of about 9 A from a 20 volt transformer. The results are assessed from the degree of fragmentation of the pipe and the caps. A DDT is considered to have occurred only if the pipe is actually fragmented into two or more distinct pieces. The tests were performed at $20° \pm 1°C$, unless otherwise indicated.

Class B: Thermal stability—explosion tests

B1. Koenen and Ide B.A.M. test

Koenen and Ide [11] developed a test method using vented containers for determining the sensitivity of the test material to a thermal stimulus. This method has been standardized as the steel case method of the B.A.M. The steel case has an interior diameter of 2.4 cm, is 7.5 cm long, and has a 0.05 cm wall thickness. The tube can be fitted and closed with a nozzle plate having a centrally located orifice for venting that may be varied from 0.1 to 2.0 cm. The test material is loaded to a height of 6.0 cm, and the case is heated externally by a uniform flow of propane gas from four burners. The maximum nozzle diameter (critical diameter) at which explosion of the material occurs is recorded, together with the time from the ignition of burners to the first visible burning of the test material out of the nozzle opening (t_1) as well as the additional time from burning to explosion (t_2). The criterion for explosion is the fragmentation of the case into several (at least three) coarse, or many small, pieces.

B2. Thermal explosion test

This test is currently under development at the Bureau of Mines Pittsburgh Research Center [12]. The test procedure is as follows: the test material is loaded into a schedule 80 steel pipe (40 cm long, 3.17 cm exterior diameter); the non-vented pipe is closed with schedule 80 caps. Two Chromel—Alumel thermocouples, encased in stainless steel, are mounted through 1.03 cm diameter pipe plugs. One is positioned at the center of the long axis of the pipe material; the other one is placed 7.5 cm from the end of the pipe. Heating is accomplished externally by a 35.5 cm long fiberglass-insulated Nichrome ribbon wrapped around the pipe. The heating rate employed is 2°C/min, which is continued until explosion or pipe failure occurs. The temperature at which explosion occurs and the degree of fragmentation serve as the criteria for judging the sensitivity of the material. In some cases this exotherm indicates the onset of a rapid reaction only, and the temperature recorded is not a "true" explosion temperature.

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*Reference to trade names does not imply endorsement by the Bureau of Mines.

Class C: Energy release tests

C1. Heavy confinement cap test

This test is under development by the E27.03 committee of the ASTM [13]. As currently stated, the test is designed to determine whether a rapid exothermic decomposition can be initiated in a chemical or a mixture of chemicals by subjecting them to high pressures and high temperatures for a very brief period of time. The method also provides a measure of the energy release. For a test, 4.0 g of the test material are placed in a 2.0 cm o.d. glass test tube, which was previously cut off to a length of 7.5 cm. The test tube is placed into a 2.54 cm diameter by 10.8 cm deep hole previously drilled in a 12.7 cm diameter by 15.0 cm high steel borehole block. A No. 8 strength seismographic-type electric detonator (Atlas Staticmaster), serving as the stimulating source, is inserted in the test tube, and the detonator leg wires are fed out of the borehole by positioning them in a groove machined on the top surface of the borehole block. At this point, a 12.7 cm diameter by 2.3 cm thick flat steel plate of mass 2.27 kg is placed and centered on top of the borehole block. The detonator is then fired, the plate is propelled upwards, and the total time of flight is measured. The maximum throw height, which is calculated from the total flight time, serves as a rough index of energy release.

C2. Ballistic mortar test

The tests were carried out in the ballistic mortar test facility described in Ref. [14]. For solid samples, a cup, 2.5 cm in diameter by 4.4 cm long, constructed from 0.0125 cm thick tinfoil is used as the container. In the case of liquids, glass containers made from preshortened, 10 ml Pyrex distilling flasks were used. A No. 8 strength electric detonator was used to initiate the charge. Granular trinitrotoluene was the reference material. The recoil of the mortar is used as a measure of the strength of the test material and is expressed relative to that of trinitrotoluene, which is taken as 100%. Three trials per test sample are performed.

C3. Underwater test method

The strength of energetic materials can also be evaluated by exploding a charge under water and measuring the shock and bubble energies. The Bureau of Mines underwater facility is 61 meters in diameter and 7.6 meters deep. The experimental details are given in Ref. [14]. These tests were performed at a depth of 3.66 meters.

In this study, the test samples, whose masses were recorded, were confined in 1000 ml spherical glass flasks. The stimulator employed was a 5.0 cm diameter pentolite sphere containing a 1.9 cm diameter by 1.9 cm long tetryl pellet initiated by a No. 8 strength electric detonator. Trinitrotoluene served as the reference material. Three trials were performed for each test material. The shock and bubble energies were calculated from oscilloscope traces and are expressed in terms relative to trinitrotoluene.

Precautions were taken during the handling of peroxides. In view of their flammability and highly reactive nature, special care was taken while handling these materials. All test components that were likely to come into contact with the peroxides were tested for compatibility. Materials that were observed to react either immediately or slowly, as detected by bubble evolution or marked increase in the temperature of the system, were not used in the test configuration. Some of the materials for which compatibility tests were performed were copper alloy (detonator case), metal pipes, igniter material, and rate probes for velocity measurement. Major incompatibility problems were observed only with hydrogen peroxide. However, these problems were circumvented by using Teflon spray (Crown #6075 dry film lubricant TFE) coating on the material used in testing. In the deflagration-to-detonation transition test and thermal explosion test, it was felt that, because of the length of the pipes, the interior of the pipes might not receive a thorough coating of teflon spray; hence, these tests were not performed with hydrogen peroxide. In the underwater method, hydrogen peroxide was observed to react with one of the organic sealants, which was replaced with a non-reactive sealant.

Most of the tests on diisopropyl peroxydicarbonate were carried out at 0°C and 5°C because this compound is known to decompose rapidly at about 20°C.

Experimental results

The experimental results presented here are introductory in nature, intended to give only a preview of the data; the results are integrated in the Discussion section.

Class A: Detonability tests

A1. Card-gap test
The test results are given in Table 2. None of the peroxides tested except diisopropyl peroxydicarbonate were shock sensitive since no damage to the witness plate was observed, and the rate probe records indicated that the detonation velocity attenuated rapidly to the sonic velocity of the material in all tests. However, it was observed that complete fragmentation of the acceptor pipe occurred in tests with the two solid organic peroxides — benzoyl peroxide and dicumyl peroxide. A few additional tests were performed with these two materials using 1.25 and 2.50 cm Plexiglas gaps. Total fragmentation of the acceptor pipe occurred in these tests also, indicating that these two materials did sustain a partial or incomplete reaction.

In the tests performed on diisopropyl peroxydicarbonate at 5°C and 10°C, the witness plates were domed, and the acceptor pipes were totally fragmented. This degree of damage is sometimes sustained when test materials undergo low-velocity detonation. It may be mentioned here that for a material to be classified as possessing significant explosive properties, positive results

TABLE 2

Results of card-gap tests

Test sample	Gap value (cm)	Velocity (m/sec)	Acceptor and plate damage	Nature of reaction
Benzoyl peroxide ($\rho = 0.46$)[2]	0	2410,950[1]	Total fragmentation. a few small and mostly large pieces; no plate damage.	All the sample reacted; reaction may be deceleratory in nature.
	1.25			
	2.50			
Dicumyl peroxide ($\rho = 0.53$)	0	3600,1700		
	1.25			
	2.50			
Diisopropyl peroxydicarbonate ($\rho = 0.66$)	0[3]	2630,2460,1560	Total fragmentation; mostly small and a few large pieces; dome in the witness plate	All the sample reacted; reaction appears to proceed in the unsteady, low-velocity detonation mode.
	0[4]	3380,1470,887		
t-Butyl perbenzoate	0	2700,1600	5.0 cm length of acceptor intact at top; no plate damage	Only part of the sample reacted; incomplete reaction.
Methyl ethyl ketone peroxide (11% AO)	0	1973,1019	10.0 cm length of acceptor intact at top; no plate damage.	
Methyl ethyl ketone peroxide (9% AO)	0	4320,1420	5.0 cm length of acceptor intact at top; no plate damage.	
Hydrogen peroxide (70%)	0	2970,1300	A few small pieces and 4 large pieces; no plate damage.	

[1] The last value refers to the velocity to which the shock wave decays in each test.
[2] Loading density of the solid sample in g/cm^3.
[3] Test temperature 5°C (sample in the solid state).
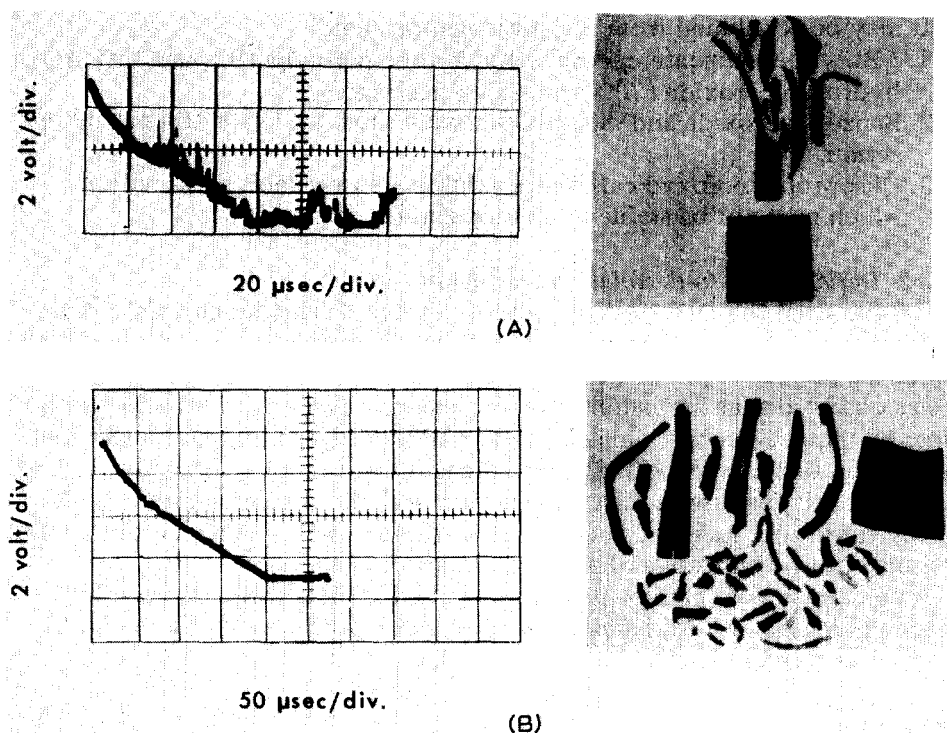[4] Test temperature 10°C (sample in the liquid state).

Fig. 1. Rate probe records and acceptor tube and witness plate damage for (A) methyl ethyl ketone peroxide (9% active oxygen), (B) diisopropyl peroxydicarbonate.

(detonation velocity > 1500 m/sec, hole in the witness plate, etc.) should be obtained at gap values of 5.08 cm or more in the card-gap test. Since the test results for IPP are not very definitive even at 0 cm gap, it is likely that this material possesses poor shock sensitivity.

Figure 1 shows acceptor pipe and witness plate damage and the corresponding rate probe record obtained for relatively high (IPP) and relatively low (MEKP 9% AO)* reactivity test materials.

Grelecki [15] in earlier studies, concluded that t-butyl perbenzoate was not shock sensitive and that a low-order detonation could be induced in benzoyl peroxide. However, his conclusions were based wholly on the fragmentation nature of the acceptor pipe, since no witness plate was used, and it is believed that the additional information obtained from a witness plate is most useful in making an evaluation. Keim [16] indicates that IPP could be detonated in a 304 stainless steel tube (6.25 cm o.d., 0.63 cm wall thickness, and 20 cm long) with a 5.0 by 2.5 cm pentolite booster at 10°C. The velocity values reported by Keim also show that the detonation is unsteady in nature and the detonation velocity decays to the sonic velocity in the test material.

*Active oxygen.

It may be concluded from our investigation that:

1. *t*-Butyl perbenzoate, methyl ethyl ketone peroxide (9% and 11% AO), hydrogen peroxide (70%) are shock insensitive.
2. Benzoyl peroxide and dicumyl peroxide show evidence of a partial reaction.
3. Diisopropyl peroxydicarbonate exhibits a low-velocity detonation, which may not be stable in its propagation characteristics.

A2. Deflagration-to-detonation transition test

Results from the DDT tests are given in Table 3. The data indicate that none of the peroxides tested, except IPP, show a tendency to undergo DDT under the present experimental conditions. In the case of dicumyl peroxide it was observed that the sample burned, leaving a black liquid residue in the pipe; the pipe, however, remained intact. IPP, on the other hand, exhibited DDT when tested with both 20 and 10 g igniters. It may be concluded, therefore, that IPP possesses a high tendency to undergo the deflagration-to-detonation transition. As mentioned in the Introduction, the end result in a DDT test may not be indicative of a true detonation in all cases.

A comparison of the pipe damage sustained in tests with methyl ethyl ketone peroxide (9% AO) and diisopropyl peroxydicarbonate in the DDT test is illustrated in Fig. 2.

TABLE 3

Results of DDT tests

Test sample	Number of fragments	Remarks
Benzoyl peroxide[1]	0	Sample burned; pipe was slightly distorted.
Dicumyl peroxide	0	Sample burned; black liquid residue.
Diisopropyl peroxydicarbonate	14[2]	Pipe ruptured into 14 pieces; 1 cap ruptured into 5 pieces; 1 cap distorted.
	6[3]	Pipe ruptured into 6 pieces; 1 cap deformed.
t-Butyl perbenzoate	0	Pipe slightly bulged at 1 end; 1 cap broke into 2 pieces.
Methyl ethyl ketone peroxide (11% AO)	0	Pipe split open; both caps remained undamaged.
Methyl ethyl ketone peroxide (9% AO)	0	Pipe slightly bulged at 1 end; 1 cap ruptured into 2 pieces.
Hydrogen peroxide (70%)	Not performed	

[1] Loading densities of the solid samples are similar to those given in Table 2.
[2] Igniter weight 20 g, test temperature 5°C.
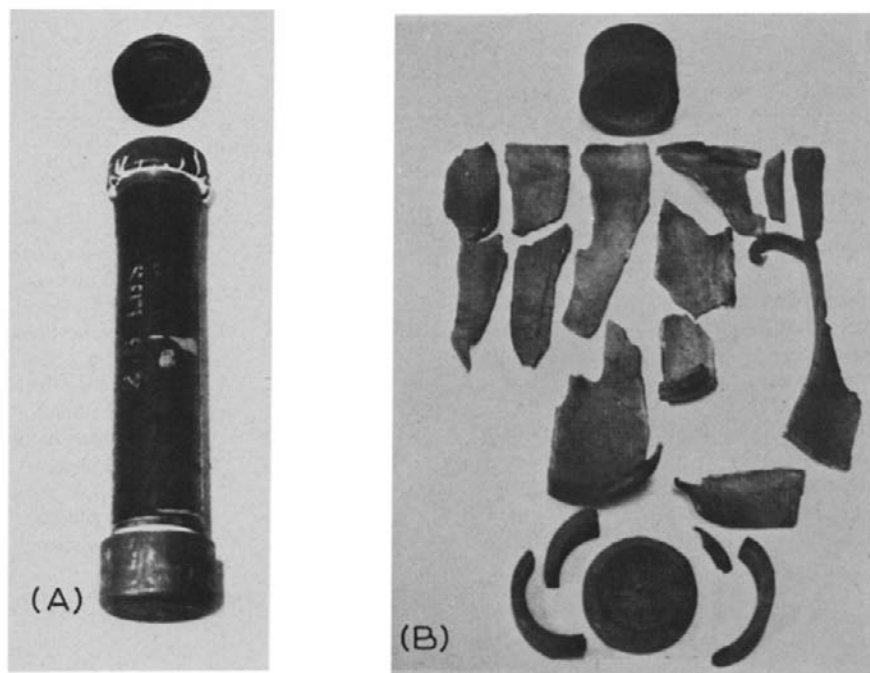[3] Igniter weight 10 g, test temperature −5°C.

Fig. 2. Pipe damage in DDT test for (A) methyl ethyl ketone peroxide (9% active oxygen), and (B) diisopropyl peroxydicarbonate (tested at 5°C with a 20 g igniter).

B. Thermal stability-explosion tests

B1. Koenen and Ide B.A.M. test

The results of this test are presented in Table 4. Dicumyl peroxide and hydrogen peroxide decomposed too slowly to produce an explosion, while the other four peroxides exhibited varying degrees of reactivity. These results indicated that the reactivities should follow the sequence
BP> IPP> BPB> MEKP (11% AO) > MEKP (9% AO) > DCP> HP. The nature of fragmentation of the steel case also provided an indication of the degree of violence associated with the explosion. When explosions were observed, the steel case was fragmented into three or four pieces.

B2. Thermal explosion test

Table 5 tabulates results of the thermal explosion test. It should be mentioned here that the explosion temperatures obtained in the present work are considerably higher ($> 40°C$), for most of the peroxides tested, than the self-accelerating thermal decomposition temperatures (SADT) reported in the literature for these compounds [1]. This may be due to the differences in the test configurations between the thermal explosion test and the conventional SADT test.

TABLE 4

Results of the Koenen and Ide B.A.M. tests

Test sample	Orifice diameter, d (mm)	t_1 (sec)	t_2 (sec)	Time function $\sqrt{t_1/d} + t_2/d$	Remarks
Benzoyl peroxide	8.0	3.5	—[1]	0.64	Steel case broke into 3 pieces.
Dicumyl peroxide	1.0	8.0	—	—	No explosion.
Diisopropyl peroxy-dicarbonate	8.0	9.0	1.0	1.18	Steel case broke into 3 pieces.
t-Butyl perbenzoate	4.0	15.0	3.0	2.15	Steel case broke into 3 pieces.
Methyl ethyl ketone peroxide (11% AO)	6.0	14.0	7.0	2.68	Steel case broke into 4 pieces.
Methyl ethyl ketone peroxide (9% AO)	1.0	18.0	10.0	14.2	Steel case broke into 4 pieces.
Hydrogen peroxide (70%)	1.0	5.0	—	—	No explosion

[1] Instantaneous explosion.

TABLE 5

Results from thermal explosion tests

Test sample	Explosion temperature (°C)	Pipe damage
Benzoyl peroxide[1]	100	None[2]
Dicumyl peroxide	160	None[2]
Diisopropyl peroxy-dicarbonate	47	1 cap off, pipe split — opened up to 15 cm from 1 end
t-Butyl perbenzoate	116	1 cap off, pipe split — opened up to 20 cm.
Methyl ethyl ketone peroxide (11% AO)	93[3]	1 cap off, pipe split — opened up to 22 cm.
Methyl ethyl ketone peroxide (9% AO)	123	Thermocouple plugs blew out, holes enlarged and pipe distorted.
Hydrogen peroxide (70%)	Not performed	—

[1] Loading densities of the solid samples are similar to those given in Table 2.
[2] Decomposition products vented through thermocouple holes; rapid exotherm before explosion or pipe failure.
[3] Sample found to be incompatible with the configuration.

The explosion temperature recorded for MEKP (11% AO) may not be as accurate as desired because significant bubble evolution was observed before the test, despite the fact that the interior of the pipe was coated with Teflon spray. Based on explosion temperature, the peroxides follow the sequence IPP > MEKP (11% AO) > BP > BPB > MEKP (9% AO) > DCP.

C. Energy release tests

C1. Heavy confinement cap test

Test results for the peroxides are found in Table 6, together with comparable values for nitromethane(NM) and trinitrotoluene (TNT). The latter two materials were included because NM is proposed as the reference material for normalizing data in the proposed ASTM standard test, but a TNT equivalent value was needed for comparing data with those obtained in another test (ballistic mortar test). It should be pointed out that plate throw heights under 1.8 meters have questionable significance since the electric blasting cap initiated in an inert test sample may produce heights of about this magnitude. Thus dicumyl peroxide, with its non-normalized value of 2.2 meters, releases very little energy.

C2. Ballistic mortar test

Results are presented in Table 7. As indicated in the Experimental section, the results here are expressed in terms of a TNT mass equivalent (% TNT). The values ranged from approximately 0% for dicumyl peroxide to 42% for hydrogen peroxide. Dicumyl peroxide apparently did not yield any net deflection after subtracting the contribution from the detonator, presumably because it was insensitive to initiation by a No. 8 strength detonator.

TABLE 6

Results of the heavy confinement cap tests

Test sample	Average[1] height (m)	Relative height (% NM)[2]	Relative height (% TNT)[3]
Nitromethane	24.5	100.0	104.7
Trinitrotoluene	21.9	90.9	100.0
Benzoyl peroxide	4.6	19.2	20.1
Dicumyl peroxide	2.2	9.08	9.51
Diisopropyl peroxy-dicarbonate	7.4[4]	30.0	33.7
t-Butyl perbenzoate	5.6	23.1	24.2
Methyl ethyl ketone peroxide (11% AO)	7.8	32.7	34.2
Methyl ethyl ketone peroxide (9% AO)	6.1	25.0	26.2
Hydrogen peroxide	6.7[5]	29.0	30.4

[1] The scatter in the test data for any particular test sample is in the range 0.1 to 0.4 m.
[2] NM — Nitromethane.
[3] TNT — Trinitrotoluene.
[4] Tested at 0°C.
[5] Data obtained by Keim [16] are higher than the value reported here.

TABLE 7

Ballistic mortar test results for peroxides

Test sample	Weight strength[1] (% TNT)
Trinitrotoluene	100
Benzoyl peroxide	15.8
Dicumyl peroxide	~ 0
Diisopropyl peroxydicarbonate	27.0[2]
t-Butyl perbenzoate	16.0
Methyl ethyl ketone peroxide (11% AO)	26.0
Methyl ethyl ketone peroxide (9% AO)	18.0
Hydrogen peroxide (70%)	42.0

[1] The maximum deviation in the swing recorded for any test sample was about 3%, except for hydrogen peroxide, which gave highly irreproducible results.
[2] Tested at 5°C.

TABLE 8

Relative bubble energy values for peroxides

Test sample	Relative energy/unit mass (% TNT)
Trinitrotoluene	100
Benzoyl peroxide[1]	42.7
Dicumyl peroxide	12.1
Diisopropyl peroxydicarbonate	36.2[2]
t-Butyl perbenzoate	6.0
Methyl ethyl ketone peroxide (11% AO)	6.5
Methyl ethyl ketone peroxide (9% AO)	3.7
Hydrogen peroxide (70%)	2.3

[1] For wet benzoyl peroxide (22% H_2O), the relative bubble energy is 28.8.
[2] Tested at 0°C.

C3. Underwater method

Table 8 gives the underwater bubble energies of the peroxides relative to the bubble energy for an equivalent mass of TNT. Although attempts were made to measure the shock energies also, the pressure profile records revealed that no measurable shock energy was released for any of the peroxides tested, other than that observed for the stimulator (booster) when it was fired by itself. This table also shows that only benzoyl peroxide and diisopropyl peroxydicarbonate yielded any substantial values for bubble energy (42.7% and 36.2%, respectively). The three liquid peroxides, t-butyl perbenzoate, methyl ethyl ketone peroxide (9% and 11% AO), and hydrogen peroxide, yielded extremely low values (2.3% to 6.5%), while dicumyl peroxide
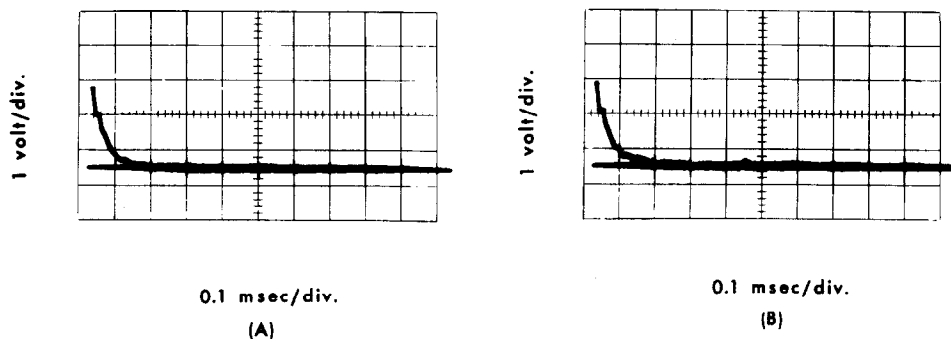
Fig. 3. Typical shock wave recording for (A) pentolite sphere, and (B) methyl ethyl ketone peroxide (9% active oxygen).

gave an intermediate value (12.1%). Typical shock energy profiles obtained in the underwater test are presented in Fig. 3 for a pentolite sphere and for methyl ethyl ketone peroxide (9.0% AO), fired by the pentolite stimulator.

Results of correlation studies

A standard multiple linear regression technique was employed to seek correlations between the experimental results (the heavy confinement cap test, ballistic mortar test, and underwater test) with the following parameters: heat of decomposition, difference between the heat of combustion and heat of decomposition, oxygen balance (values obtained from the CHETAH program), and explosion gas volume (estimated from the decomposition products predicted by the CHETAH program)*. Table 9 is a tabulation of the CHETAH criteria values and gas volumes for the six peroxides as well as those for nitromethane and trinitrotoluene. The table also gives the hazard ratings (H = high, M = medium, L = low) for all the test materials.

The correlation analysis was carried out using the test result from the energy release tests (Class C) as the dependent variable, and the three CHETAH criteria together with gas volume (given in Table 9) as the independent variables, either singly or in several combinations. The results of the study are presented in Table 10, where results are shown for the runs that yielded the best correlations among the several combinations attempted. The multiple correlation coefficients obtained ranged from 0.922 to 0.999.

Table 11 compares the experimentally obtained bubble energies with corresponding estimated values from the linear regression line. As may be seen, agreement between experimental and predicted values is quite good.

At first glance the results from the correlation studies might lead one to conclude that the correlation between test results and the criteria of choice

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TABLE 9

CHETAH program results

Test sample	CHETAH criteria[1,2]			
	ΔH_d (kcal/g)	$\Delta H_c - \Delta H_d$ (kcal/g)	OB (%)	Gas volume (moles/g)
Trinitrotoluene	−1.41 (H)	−2.17 (H)	−74.0 (H)	0.0253
Nitromethane	−1.51 (H)	−1.16 (H)	−39.3 (H)	0.0368
Benzoyl peroxide	−0.74 (H)	−5.64 (L)	−191.6 (M)	0.0186
Dicumyl peroxide	−0.66 (M)	−7.89 (L)	−266.3 (L)	0.0240
Diisopropyl peroxy-dicarbonate	−0.57 (M)	−3.89 (M)	−131.9 (M)	0.0315
t-Butyl perbenzoate	−0.69 (M)	−6.33 (L)	−214.2 (M)	0.0257
Methyl ethyl ketone peroxide (11% AO)	−0.84 (H)	−4.54 (M)	−153.9 (M)	0.0297
Methyl ethyl ketone peroxide (9% AO)	−0.77 (H)	−4.60 (M)	−156.3 (M)	0.0279
Hydrogen peroxide (70%)	−0.52 (M)	0 (H)	32.9 (H)	0.3080

[1] ΔH_d: Heat of decomposition; $\Delta H_c - \Delta H_d$: Heat of combustion − heat of decomposition; OB : Oxygen balance.
[2] Letters in parentheses indicate hazard rating : H: High; M: Medium; L: Low.

(ΔH_d, $\Delta H_c - \Delta H_d$, OB, and GV) is poor since the standard errors of estimation are generally high. However, the multiple correlation coefficient is close to unity in all cases, and the T-ratios (an indicator of the reliability of the coefficients, not reported in Table 10) of the various coefficients are quite high in most of the runs. Typical values of the T-ratios are as follows: run no. 4: $\Delta H_d = 11.1$; GV = 5.99; OB = 4.88.

Several factors may have contributed to the large errors of estimation. They are (1) insufficient number of observations, (2) scatter in experimental data, and (3) improper choice of independent variables. Despite these shortcomings, the following remarks seem appropriate:

1. No correlation is observed between the experimental test results and ΔH_d or $\Delta H_c - \Delta H_d$ when either is used individually.

2. Acceptable correlations can be realized using a combination of ΔH_d and $\Delta H_c - \Delta H_d$ as the independent variables. Inclusion of oxygen balance and/or gas volume further improves the correlation for results from the heavy confinement cap test and ballistic mortar tests.

3. The correlation between bubble energy (using all six peroxides in the analysis) and the independent variables is extremely poor (multiple correlation coefficient is 0; standard error of estimation is 1162%). However, the data in Table 10 clearly show that a marked improvement in the correlation coefficient is obtained when t-butyl perbenzoate, methyl ethyl ketone peroxide (9% and 11% AO), and hydrogen peroxide − found to be shock insen-

TABLE 10

Results of multiple linear regression analysis

Test	Dependent variable	Coefficients for independent variables[1]					Multiple correlation coefficient	Standard error of estimation (%)
		Constant	ΔH_d	$\Delta H_c - \Delta H_d$	OB	GV		
Heavy confinement cap test	Average height	—	−53.99	6.854	−9.294	—	0.992	27.4
Ballistic mortar[2] test	Weight strength (% TNT)	−29.58	−71.93	−17.63	55.26	—	0.994	24.9
		−142.0	−151.5	—	−0.208	363.5	0.998	6.41
Underwater method[3]	Relative energy/unit mass	−115.2	−115.2	—	—	174.0	0.996	18.9
		1.004	−0.1708	0.1254	—	—	0.999	6.43

[1] ΔH_d: Heat of decomposition; $\Delta H_c - \Delta H_d$: Heat of combustion − heat of decomposition; OB: Oxygen balance; GV: gas volume.
[2] Does not include dicumyl peroxide.
[3] Includes only benzoyl peroxide, dicumyl peroxide, diisopropyl peroxydicarbonate, and trinitrotoluene.

TABLE 11

Comparison of experimental and predicted relative bubble energy values

Test sample	Experimental relative bubble energy[1]	Predicted[2] relative bubble energy
Benzoyl peroxide	42.7	42.3
Dicumyl peroxide	12.1	12.7
Diisopropyl peroxydicarbonate	36.2	36.0
Trinitrotoluene	100.0	97.3

[1] Relative energy/unit mass (% TNT).
[2] Estimates from the linear regression analysis.

sitive in test A1 — are eliminated from consideration. The correlation coefficient is now a respectable 0.999. However, this result may not be statistically significant in view of the fact that the number of observations is small. The point here is that some relatively shock insensitive test materials are not sufficiently stimulated under the light confinement conditions that exist in the underwater test, and these test materials release very little energy. Preliminary data from the gap test can be useful in identifying the insensitive materials.

Discussion

One major objective of this effort was to identify the tests that might yield information useful in evaluating the potential hazards of organic peroxides. As stated in the Introduction, the tests are divided into three categories:
    A. Detonability tests.
    B. Thermal stability-explosion tests.
    C. Energy release tests.
The results of the detonability tests are discussed first. In this section, the discussion is restricted to organic peroxides. Both the card-gap test and the deflagration-to-detonation transition test show that benzoyl peroxide, dicumyl peroxide, t-butyl perbenzoate, and methyl ethyl ketone peroxide (9% and 11% AO) are not detonable; diisopropyl peroxydicarbonate, however, did appear to reveal possible low-velocity detonable properties in the gap test. Results of the DDT test, however, unambiguously demonstrated that IPP possesses a potential detonation hazard since it gave a positive result even when tested with a 10 g igniter at $-5°C$.

In addition, results of another study [4] are in agreement with those given here. Very few commercial organic peroxides have been known to exhibit detonation potential except IPP and some MEKP solutions. Although

most of the organic peroxides exhibited a low sensitivity to shock, it appeared that the detonability tests (category A) could provide useful information, especially when dealing with new compounds.

The thermal stability-explosion test results can be summarized as follows: both tests in this study, the Koenen and Ide B.A.M. test and the thermal explosion test, provide clear insight into the thermal ignition properties of the organic peroxides. Based on the time-function parameter (as defined in Table 4) obtained from the former test, the peroxides can be arranged in the following order of decreasing reactivity: BP > IPP > BPB > MEKP (11% AO) > MEKP (9% AO) > DCP. Similarly, the explosion temperature recorded in the thermal explosion tests enables one to place the peroxides in the following order of reactivity: IPP > MEKP (11% AO) > BP > BPB > MEKP (9% AO) ≥ DCP.

Attempts to better understand the results obtained in the reactivity tests were made by considering the three CHETAH criteria results, as well as the active oxygen content of the materials. The test materials are ordered on the bases of active oxygen content and oxygen balance below:

Active oxygen content: MEKP(11.0) > MEKP(9.0) > BPB(8.2) > IPP (7.5) > BP (6.6) > DCP (5.9)

Oxygen balance: IPP(−131.9) > MEKP(11.0% AO)(−153.9) > MEKP(9% AO) (−156.3) > BP(−191.6) > BPB(−214.2) > DCP(−266.2).

Neither of these two orderings agrees well with those obtained using results of the two reactivity tests.

In view of these apparent non-correlations, a standard multiple regression technique, similar to that applied to results of the energy release tests, was employed, using various combinations of the three CHETAH criteria, as well as active oxygen content as the independent variables. Results of this analysis summarize as follows:

1. The values obtained for the time function from the Koenen and Ide B.A.M. tests on peroxides do not correlate well with either oxygen balance

TABLE 12

Comparison of experimental and predicted thermal explosion temperatures

Test sample	Experimental explosion temperature (°C)	Predicted[1] explosion temperature (°C)	% error[1]
Benzoyl peroxide	101	103.2	2.2
Dicumyl peroxide	160	155.1	−3.1
Diisopropyl peroxydicarbonate	47	46.4	−1.2
t-Butyl perbenzoate	116	123.3	6.3
Methyl ethyl ketone peroxide (9% AO)	123	119.0	3.3

[1] Estimates from linear regression analysis.

or active oxygen content of the peroxides. However, inclusion of ΔH_d and $\Delta H_c - \Delta H_d$ along with oxygen balance significantly improved the correlation (multiple correlation coefficient -0.88). It was also noted that the combination of independent variables ΔH_d, $\Delta H_c - \Delta H_d$, and OB gave a much better correlation than the combination ΔH_c, $\Delta H_c - \Delta H_d$, and AO. A multiple correlation coefficient 0f 0.88 was obtained in the former case, compared with 0.52 in the latter case.

2. Results of the thermal explosion test appear to correlate progressively better as one includes more of the independent variables in the analysis. This is demonstrated below:

Independent variable(s)	Multiple correlation coefficient
AO	0.24
OB	0.83
AO and OB	0.90
ΔH_d, OB, and AO	0.94
ΔH_d, $\Delta H_c - \Delta H_d$, and AO	0.95
ΔH_d, $\Delta H_c - \Delta H_d$, and OB	0.99

Note that a somewhat better correlation was obtained using oxygen balance in combination with ΔH_d and $\Delta H_c - \Delta H_d$ rather than using active oxygen content as the additional independent variable. Active oxygen content proved to be the poorer independent variable in the correlation in the Koenen and Ide B.A.M. test also. Thus, for reasons not clear, the results of the thermal explosion test correlated better with the independent variables used in this analysis than did those from the Koenen and Ide B.A.M. test.

Table 12 shows a comparison of the experimental and predicted thermal explosion temperatures using ΔH_d, $\Delta H_c - \Delta H_d$, and OB as the independent variables. The maximum percentage difference between any experimental and predicted value occurred for t-butyl perbenzoate, and was only 6.3%.

In addition to giving a better understanding of the relative reactivity of peroxides, the thermal tests performed also indicated that the minimum thermal explosion risk was for dicumyl peroxide. Thus, it appears that the Koenen and Ide B.A.M. test and thermal explosion test, in addition to providing insight into the relative thermal explosion hazards of peroxides, also enable one to differentiate between compounds that have potential explosion characteristics and those that are essentially non-explosive in nature.

The tests described under categories A and B, namely detonability and thermal stability-explosion tests, have been found to be helpful in tentatively classifying the five organic peroxides into three classes: (1) Compounds that may pose a detonation hazard, e.g., diisopropyl peroxydicarbonate, (2) compounds that possess potential deflagration properties, e.g., benzoyl peroxide, t-butyl perbenzoate, and methyl ethyl ketone peroxide (9% and 11% AO), and (3) compounds that may possess only fire hazard potential, e.g., dicumyl peroxide. It should also be pointed out here that the tentatively

proposed classification system is still an arbitrary one and should be supplemented by information from other hazard evaluation tests such as measurements of the flash point temperatures (for liquid peroxides) and impact sensitivity and friction sensitivity tests. In addition, the present study needs to be extended to examine the hazard characteristics of additional peroxides to determine whether it would be feasible to assign these compounds to one of the three classes proposed.

The energy release tests were performed with the aim of gaining perspective on the energy release of organic peroxides relative to that of the reference material, trinitrotoluene. To the best of the authors' knowledge, comparable data of this type have not been gathered previously.

The results of the heavy confinement cap test and ballistic mortar test will be discussed first. Based on the relative energy measured (with trinitrotoluene as the reference material), the organic peroxides are ordered as follows: MEKP (11% AO) > IPP > MEKP (9% AO) > BPB > BP > DCP. It should be pointed out here that it may not be appropriate to arrange the peroxides in any particular order of either increasing or decreasing strength, since the measured strength values in some cases were not sufficiently different to distinguish one from another; this point is clearly evident by examining the data in Tables 6 and 7. Therefore, the order given is offered as a rough index of the relative energy release of the various peroxides tested. It is interesting to note that in both these tests, the ordering and magnitude of the relative strength values were roughly similar. For example, IPP had a value of 33.7% relative height in the heavy confinement cap test as opposed to 27.0% relative weight strength in the ballistic mortar test. This may be rationalized by considering the computed maximum heat of decomposition and the difference in the heat of combustion and heat of decomposition values from the CHETAH program. In fact, there is better agreement between the test results and the $\Delta H_c - \Delta H_d$ values than between the test results and the ΔH_d values.

ΔH_d : MEKP(11% AO)(−0.84) > MEKP(9% AO)(−0.77) > BP (−0.74) > BPB (−0.69) > DCP (−0.66) > IPP (−0.57)

$\Delta H_c - \Delta H_d$: IPP(−3.89) > MEKP(11% AO)(−4.54) > MEKP(9% AO) (−4.60) > BP (−5.64) > BPB (−6.33) > DCP(−7.89).

Results of energy measurements from the underwater test method do not correlate well with results from the other two energy release tests. First, none of the peroxides tested gave any appreciable values for the shock energy (i.e., the shock profiles for the booster and booster-test material combination were almost identical). The relative bubble energy values are ordered as follows: BP > IPP > DCP > MEKP (11% AO) > BPB > MEKP (9% AO). Strictly speaking, only the three solid peroxides, namely benzoyl peroxide, diisopropyl peroxydicarbonate, and dicumyl peroxide, had significant bubble energy values. The bubble energy values obtained correlate, in a sense, with the card-gap test results. Only those peroxides that exhibited reactive characteristics in the shock sensitivity test gave appreciable values for the relative bubble energy in the underwater test. Thus, BP, IPP, and DCP, which might have detonated "parti-

ally" in the former test, were found to possess significant bubble energies, while the other peroxides, BPB and MEKP (9% and 11% AO), which were apparently shock insensitive, yielded low relative bubble energy values. The correlation studies also appear to confirm this. Two possible factors that may account for the differences in the behavior of peroxides in the underwater test compared with that in the other two energy release tests are the stimulator-acceptor ratio and the degree of confinement. Although the stimulator (booster) used in the underwater test contained more high explosive than the stimulator (No. 8 strength electric blasting cap) used in the ballistic mortar and heavy confinement cap tests, the ratios of the stimulator mass to test sample mass were roughly the same in all three tests. In fact, several underwater experiments were performed with test samples comparable to that used in the other two tests. The stimulator used in these small-scale underwater tests was a No. 8 strength electric blasting cap, and these results are shown below:

Test material	Scale size*		Relative energy/unit mass**
	(ml)	(g)	
Benzoyl peroxide	5	2.90	0.30
Methyl ethyl ketone peroxide (11% AO)	5	5.95	0.028

When the results presented above are compared with those in Table 8, it may be seen that the results for MEKP (11% AO) and BP stand roughly in the same ratio. Thus, the different stimulators used in the different strength tests are not believed to be a pertinent factor. This, then, leads one to differences in confinement. In the underwater test, there is no rigid confinement since the test material is contained in a glass flask. Hence, in the underwater test, the energy release characteristics are most likely to be affected by sensitivity of the test material, while in the other two energy release tests, relatively insensitive test materials release significant energy under the existing heavier confinement conditions.

One other difference in underwater test results, relative to test results from the other two energy release tests, is the reversal in the order for IPP and benzoyl peroxide where IPP produced the lower value in the underwater test. The reasons for the reversal are not entirely clear.

Results of the explosion strength tests indicate that, in general, the peroxides can be considered to be low-strength materials — especially DCP, BPB, and MEKP (9% and 11% AO). The strength values obtained for these materials are quite similar to that obtained for a well-known nonexplosive material — ammonium nitrate.

In addition to the six organic peroxides, one inorganic peroxide, hydrogen

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*Test samples were confined in spherical glass flasks; stimulator was the Atlas Staticmaster No. 8 strength electric blasting cap.
**Energies are relative to that obtained for the stimulator.

peroxide (70% solution), was investigated. Results from both the card-gap and the Koenen and Ide B.A.M. tests lead to the conclusion that the 70% hydrogen peroxide solution is relatively less hazardous than any of the organic peroxides. However, in the energy release tests C1 and C2, this material was found to possess a high relative strength value. Presumably, this could be because of its positive oxygen balance and large gas volume of explosion products. However, it produced a very low relative bubble energy value, as may be expected, considering its insensitivity to shock in the card-gap test. Hydrogen peroxide (70% solution) appears to serve as an interesting example of a material that appears to have a low hazard potential but is nevertheless capable of releasing large amounts of energy under "extreme" test conditions. This also indirectly points out the value of performing energy release tests on compounds such as organic peroxides, since these tests give a fairly good indication of the "damage potential". The heavy confinement cap test and ballistic mortar test may be viewed as providing an "upper limit" value for damage potential, whereas the underwater method provides the "lower limit" value.

Conclusions

An attempt was made to investigate the hazard potential of organic peroxides using tests directed towards evaluating their shock sensitivity, thermal stability, and energy release properties. It appears that the tests outlined in this paper do offer a fairly comprehensive overview of the hazard characteristics of these compounds. Furthermore, the test results obtained indicate that a three-category hazard classification scheme could possibly be constructed for classifying these materials. However, in view of the fact that this study included only five peroxides, it should be cautioned that additional test materials should be examined to better assess the validity of the proposed scheme. Lastly, it is recommended that the materials be subjected to energy release tests, since they provide valuable information and can be very useful in making the total damage potential assessment.

Acknowledgements

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