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Letter to the Editor

Response to comments for thermal explosion and runaway reaction simulation of lauroyl peroxide by DSC tests

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Comments from Prof. Malow	Response
1. LPO is not an oxidizing agent, the oxygen balance is negative. For a complete LPO is not an oxidizing agent, the oxygen balance is negative. For a complete combustion reaction oxygen from other sources is necessary. The oxygen–oxygen bond only rarely decomposes to give free oxygen. It should be noted that organic peroxides and strong oxidizers are not compatible.	1. Thank you very much for reminding us. 2. Oxygen balance (OB or OB%) is an expression that is used to reveal the degree to which an explosive or reactive chemical can be oxidized. Although the oxygen balance of LPO is negative, a DSC test in different scanning rates demonstrates that heat energy increases constantly which results in a runaway reaction.
2. The TMR seems to be very short. In our laboratory, we have performed thermal stability investigations of 20 kg LPO. It took days to heat this quantity from 20 to 45 °C and the substance was thermally stable for at least 7 days at this temperature.	1. Regarding the TMR, our experimental approach was DSC testing. As you know, the DSC testing condition is in a smaller size cell (in “mg” level) than a 20-kg scale. Therefore, there are originally some differences of LPO detections between the DSC and in a 20-kg scale test.
	2. In addition, the results from DSC were based upon the simulation, and obtained from the software. In our study, the adjustment factors are heat transfer area, size, and material. Those three factors will affect the results under different transfer heat and thermal conductivity as well.
3. LPO is a solid substance as the authors rightly stated. Nevertheless they assumed that the peroxide decomposes from the liquid state even below the melting point. To our opinion, it is not advisable to neglect the melting as it can act as a thermal barrier.	1. As for the “liquid testing”, we assumed the testing was in our experimental scenario. Since our experimental measurements were all made at high temperature, the original material will be deformed or phase changed from solid into liquid. Therefore, we deliberately regarded the testing scenario as “liquid condition”.

The authors’ response to comments from Professor M. Malow on “Thermal explosion and runaway reaction simulation of lauroyl peroxide by DSC tests” at J Therm Anal Calorim (2009) 98:885–886, DOI 10.1007/s10973-009-0534-1.

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Comments from Prof. Malow	Response
4. The authors detected the melting point at 40 °C. Li and Koseki [3] detected the melting point of LPO at about 48 °C. Both temperatures are higher than 38 °C which is the maximum ambient temperature recommended by the authors. On the other hand the authors calculated a TMR of 11.6 min for a cylinder of 0.79 m^3 at 37 °C storage temperature. Li and Hasegawa proposed two different decomposition kinetics from the solid and the liquid state. Their finding that the "Thermo-chemical reactivity of LPO in solid phase was feeble" is contrary the results the authors presented.	1. From the public announcement of "Institute of Occupational Safety and Health (IOSH)" in Taiwan, it proclaims SADT of LPO is 28.6 °C, as shown in Table 1 [1–5]. 2. The mission of the Institute of IOSH Taiwan, a research agency under the Council of Labor Affairs, Executive Yuan, is to apply the scientific method in the study of various risk factors in the work environment, strictly for labor safety and health.
5. The thermal stability of LPO has been investigated intensively in the past but no corresponding literature has been cited by the authors. A comparative discussion with this literature e.g. on the sensitivity of the methods would have been useful.	1. With respect to the missing references, we will be sure to cite those papers in our future studies.
6. The deviation between the experimental kinetic parameters presented in Table 5 is considerably high and therefore an indication of a relatively high uncertainty. This of course is reflected in the thermal simulations. This should have been discussed by the authors.	1. We sincerely appreciate the comments which can help us to improve the content as well as the quality of the above article.
7. According to the international transport regulations LPO is classified as solid organic peroxide (UN 3106). The packing instructions allow transporting a maximum net mass of 50 kg in "soft" packagings. The assumption of the authors that LPO would start to decompose perceptible at ≤38 °C is totally contrary to all experiences concerning transport and storage. Explosions or thermal runaway reactions may only occur if fundamental guidelines concerning the safe handling of organic peroxides are not followed.	1. In another investigation for LPO in Taiwan [6], simulations were performed of thermal explosion under solid and liquid situation stored in various barrel shapes, such as sphere, slab, cylinder, and box under thermal explosion level. Via thermal explosion simulation, the results showed that SADT, control temperature, and emergency temperature of LPO were 19–38 °C, −1 to 28 °C, and 9–33 °C, respectively. 2. The International Chemical Safety Cards from National Institute for Occupational Safety and Health (NIOSH) showed LPO has to prevent warming above 25 °C [7].

Table 1 SADT of organic peroxides [1–5]

Content (wt%)	Chemical name	SADT (°C)
30	Di-isobutanoyl peroxide	−10.7
75	Cumyl peroxyneodecanoate	7.8
70	2,4,4-Trimethylpentyl-2-peroxyneodecanoate	9.3
75	*tert*-Amyl peroxyneodecanoate	10.8
95	bis(4-*tert*-Butylcyclohexyl) peroxydicarbonate	17.4
75	bis-(2-Ethylhexyl) peroxydicarbonate	15.4
95	*tert*-Butyl Peroxyneodecanoate	12.7
50	Di-butyl peroxydicarbonate	15.1
94.5	Dicetyl peroxycarbonate	19.9
96	Dimyristyl peroxydicarbonate	19.2
75	*tert*-Amyl peroxypivalate	21.6
75	*tert*-Butyl peroxypivalate	23.1
75	bis(3,5,5-Trimethylhexanoyl) peroxide	26.9
99	Di-lauroyl peroxide	28.6
98.5	Di-decanoyl peroxide	31.0
98	2,2′-Azo-bis-(isobutyronitrile)	37.4
98	2,2′-Azo-bis-(methylbutyronitrile)	31.8
90	2,5-bis-(2-ethylhexanoylperoxy)-2,5-dimethylhexane	38.6
90	*tert*-Amyl peroxy-2-ethylhexanoate	38.3
75	Di-benzoyl peroxide	34.1
97	*tert*-butyl peroxy-2-ethylhexanoate	36.0
96	*tert*-butyl peroxy diethylacetate	39.5
65	1,4-bis-(tert-butyperoxycarbo) cyclohexane	42.8
75	*tert*-Butyl peroxyisobutane	42.9
90	1,1-bis(*tert*-Butylperoxy)-3,3,5-trimethyl cyclohexane	50.2
50	1,1-bis(*tert*-Butyperoxy) cyclohexane	60.0
97	*tert*-Butyl peroxy-3,5,5-trimethylhexane	58.6
50	2,2-bis(*tert*-Butylperoxy) butane	64.4
75	*tert*-Butyl peroxy isopropylcarbonate	62.2
95	*tert*-Butyl peroxy-2-ethylhexyl carbonate	64.7
50	*tert*-Butyl peroxyacetate	61.2
98	*tert*-Butyl peroxybenzoate	65.8
90	Di-tertamyl peroxide	70.4
99	Dicumyl peroxide	77.8
96	bis(*tert*-Butyl peroxyisopropyl) benzene	80.8
92	2,5-bis-(t-Butylperoxy) 2,5-dimethyl-3-hexane	80.7
90	*tert*-Butyl cumyl peroxide	77.1
85	2,5-bis-(t-Butylperoxy) 2,5-dimethyl-3-hexyne	84.8
99	Di-*tert*-butyl peroxide	80.9
50	Di-isopropyl benzene monohydroperoxide	85.7
80	Cumyl hydroperoxide	84.3
98	*tert*-Butyl hydroperoxide	120.4
98	3,4-Dimethyl-3,4-diphenylhexane	158.6
95	2,3-Dimethyl-2,3-diphenylbutane	196.5

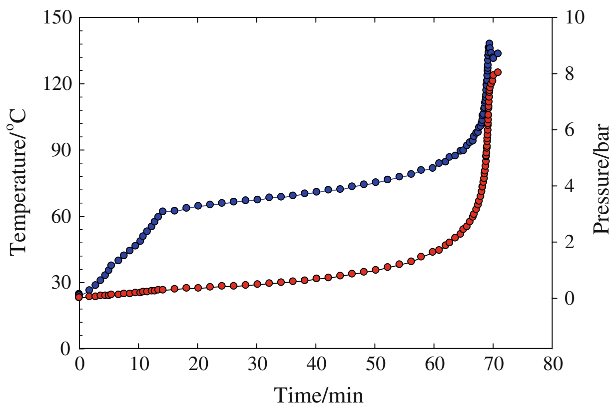

Fig. 1 LPO 40 mass% runaway by VSP2

Figure 1.

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