



FOCUS ARTICLE

## HAVE YOU ASSESSED YOUR POLYMERISABLE SUBSTANCES AND MIXTURES FOR UN TRANSPORT CLASSIFICATION?

Unsaturated organic compounds (alkenes) are common place in the chemical sector as reactive and versatile raw materials (“building blocks”) and products. Some materials are intentionally polymerised to make plastics and resins whilst others have polymerisation as an undesirable side reaction. Historically, the polymerisation behaviour of such materials has not been the subject of any transport classification regime – until now. These materials are now subject to potential classification as polymerisable substances and manufacturers and distributors have a legal obligation to consider this classification. The impact for businesses is explored in this paper.

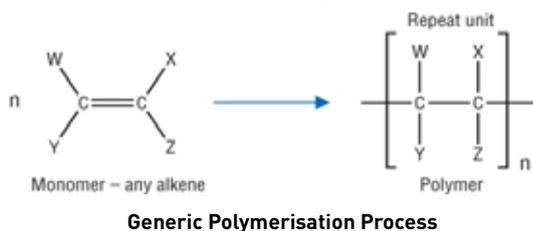
## BACKGROUND INFORMATION ON RECENT CHANGES

The latest (19th) edition of the UN Transportation of Dangerous Goods Recommendations incorporates a new UN 4.1 classification for substances that may polymerise exothermically during transport conditions. Four new generic UN numbers are added for classification of qualifying substances:

- UN3531 Polymerising substance, solid, stabilised, n.o.s. (not otherwise specified)
- UN3532 Polymerising substance, liquid, stabilised, n.o.s.
- UN3523 Polymerising substance, solid, temperature controlled, n.o.s.
- UN3524 Polymerising substance, liquid, temperature controlled, n.o.s.

## WHO IS IMPACTED?

This change brings in a whole host of unsaturated alkenic materials that hitherto may have been unclassified for transport. This will include materials ultimately intended for polymerisation – monomers, bisomers and multifunctional monomers – but also unsaturated substances not necessarily intended for polymerisation. The impact for industry is consequential given the scale of manufacture, use and transport of such materials.



On a more positive note, there are exemptions as inclusion is limited to substances and mixtures that meet the following criteria:

1. Their self-accelerating polymerisation temperature (SAPT) is 75°C or less under the conditions (with or without chemical stabilization as offered for transport) and in the packaging, IBC or portable tank in which the substance or mixture is to be transported;
2. They exhibit a heat of reaction of more than 300 J/g; and
3. They do not meet any other criteria for inclusion in Classes 1-8\*.

A mixture meeting the criteria of a polymerising substance shall be classified as a polymerising substance of Division 4.1.

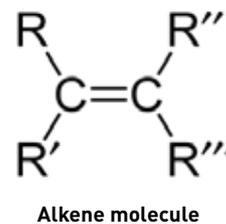
## HOW DO I ASSESS MY SUBSTANCES?

The formal test protocol which will be detailed in the next revision of the UN Manual of Tests and Criteria (MTC) is planned to be identical to that for UN 4.1 Self-Reactive Substances (ie. substances with a measured self-accelerating decomposition temperature (SADT) of 75°C or less for a 50 kg package).

Reviewing classification for an inventory of materials requires a multi-step, systematic approach which reliably identifies candidates and eliminates other substances. Our recommended approach – which maximises efficiency – is as follows:

### Step 1: Desktop Assessment of “Polymerisability”

Typically, alkene and alkyne substances with unsaturated carbon-to-carbon bonds are capable of polymerisation. Whilst other energetic functional groups will impart explosive / decomposition behaviour, such as the nitro (-NO<sub>2</sub>) group, such substances should be evaluated as self-reactive substances rather than polymerisable substances. An inspection of molecular structure should readily identify alkene and alkyne unsaturated functional groups in compounds / mixtures as candidates.



### Step 2: Estimation of Heat of Polymerisation

The heat of polymerisation of the alkene functional group is known from the literature to be in the range -50 to -90 kJ.mol<sup>-1</sup> (for alkyne functions, the value is higher at -120 to -170 kJ.mol<sup>-1</sup>). This value can be combined with the number of alkene groups and molecular weight to evaluate the heat of polymerisation in J.g<sup>-1</sup>. In the absence of other energetic functional groups, the heat of decomposition of each substance can therefore be estimated from:

$$\Delta H = \frac{\Delta H_{\text{alkene}} \times N_{\text{alkene}}}{(\text{Mol wt})}$$

Where

$\Delta H$  = Heat of reaction of the molecule (in J.g<sup>-1</sup>)

$\Delta H_{\text{alkene}}$  = Heat of reaction of alkene functional group (50000 - 90000 J.mol<sup>-1</sup>)

$N_{\text{alkene}}$  = Number of alkene groups in molecule

Mol wt = Molecular weight of the substance (in g.mol<sup>-1</sup>)

\* (author note: substances liable to decomposition or polymerisation in any other class (1-8) are prohibited from transport unless the necessary precautions have been taken to prevent the possibility of a dangerous decomposition or polymerization under normal conditions of transport).

Where the heat of reaction is  $<300 \text{ J.g}^{-1}$ , the substance or mixture can be scientifically exempted from UN 4.1 Polymerising substances classification. From the equation above, it is clear that smaller molecular weight substances will be more likely to be candidates than molecules of higher molecular weight. The presence of "inert" unreactive compounds in mixtures will also dilute the effect of unsaturation.

### Step 3: Physical Testing of Heat of Polymerisation for Candidates

If the heat of reaction / polymerisation is  $>300 \text{ J.g}^{-1}$ , physical testing is proposed to evaluate the actual heat. Differential Scanning Calorimetry (DSC) is an ideal tool for accurate quantification of reaction heat and verification of the resultant polymerisation heat against the  $300 \text{ J.g}^{-1}$  criteria.



TA Instruments DSC25 Unit

### Step 4: Self-Accelerating Polymerisation Temperature (SAPT) Determination

If the compound or mixture has a heat of polymerisation of  $>300 \text{ J.g}^{-1}$ , then formal evaluation of the SAPT is required as a final entry requirement. Some substances will only exhibit polymerisation reaction at higher temperatures, well in excess of  $75^\circ\text{C}$  and these can usually be evaluated and eliminated. Preliminary Differential Thermal Analysis (DTA) or Adiabatic Calorimetry can be used as a pre-screen for exemption – providing a suitable and sufficient safety margin or mathematical model can reliably demonstrate that the large scale onset temperature will be considerably above  $75^\circ\text{C}$ .

For formal classification required if the SAPT is suspected to be in the region of  $75^\circ\text{C}$  or below, the UN H series of tests are prescribed for SADT, and now SAPT, determination. These tests, or at least H.2 to H.4 where kinetic data obtained in small scale tests is extrapolated to the packaged item, work well for simple kinetic processes which obey Arrhenius kinetics (zero and first order reactions typically associated with decomposition processes such as organic peroxide decomposition).

However, for complex thermally initiated free-radical polymerisation of monomers, the extrapolations are far from accurate owing to the pseudo-autocatalytic nature of the chemical transformation. The presence of inhibitors is also a factor as, for true inhibitors, the period of inhibition is proportional to storage temperature and storage duration. These factors make utilisation of the H.2 to H.4 methods relatively inaccurate for SAPT evaluation. The H.1 test provides a direct package test option which eliminates the need for data extrapolation – but the test is only really practical for smaller packages. On this basis, we fully expect changes to the tests and criteria for SAPT as more reliable techniques for small scale evaluation are defined. In the medium term, transporters of potential polymerisable substances will need to adhere as closely as possible to the prescribed methods whilst taking account of the vulnerabilities of some of the methods available and commonly employed.

## CHALLENGES AND COMPLICATIONS WITH THE NEW REGULATIONS

Some inconsistencies and challenges with the new regulations are already evident and may prompt some short-term changes. The concept of SAPT has been translated 1:1 from the SADT concept associated with organic peroxides. This is not entirely appropriate as organic peroxides are not normally stabilized and the kinetics of their decomposition is described by much simpler Arrhenius models than that for polymerisation. The result of an SAPT test will therefore depend, to a great extent on the inhibitor concentration and also to some extent on the age and thermal storage history of the material. A further contradiction / complication is that the new classification does not apply to substances that are classified otherwise (for example, already classified as class 3 or 8). If a monomer that is already classified as toxic, there is no formal requirement to determine the SAPT – despite the fact that it may be very unstable. Even if SAPT is not required for transport classification, our recommendation is that it should at least be addressed somewhere in the SDS.

## HOW DEKRA CAN HELP

Our process safety specialists and fully equipped transportation safety testing laboratory facilities can guide you through the process of review of candidates and classification testing. With qualified Dangerous Goods Safety Advisors also within the team, you can also be sure of the quality of advice and support you will receive.



### DR. STEPHEN ROWE

Stephen Rowe manages the activities of the UK headquarters of DEKRA Process Safety (Chilworth Technology Ltd). He has a career background in the assessment of chemical reaction hazards and the laboratory assessment of a full range of process safety hazards including dust, gas and vapour flammability and explosives characterisation. He is an experienced trainer and regular contributor to national and international process safety conferences and symposia. As a manager, Stephen Rowe focuses on building successful teams and growing the organisation in a customer-centric manner. He oversees and is actively engaged in the company's quality and safety management systems (ISO9001 and OHSAS18001).



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### ABOUT DEKRA INSIGHT

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- Behavioural Reliability – Assuring unwavering execution of safety systems and processes
- Governance & Capabilities – Providing the framework for safety execution and results
- Safety Resource Optimisation – Putting your resources to work for safety
- Management Systems – Developing and aligning the systems that drive safety excellence
- Data Analytics & Metrics – Information and insight that drive results
- Process Safety Lab Testing – Precise data, analysis and tools for process safety decision and action
- Process Safety Engineering – Engineering and advice for process safety excellence everywhere

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[www.chilworth.co.uk](http://www.chilworth.co.uk)

[info-uk@chilworthglobal.com](mailto:info-uk@chilworthglobal.com)

[process-safety@dekra.com](mailto:process-safety@dekra.com)