Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

10 June 2015

Sub-Committee of Experts on the Transport of Dangerous Goods

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Item 3 of the provisional agenda
Listing, classification and packing

Additional criteria for polymerizing substances

Transmitted by the European Chemical Industry Council (CEFIC)

Introduction

1. During the last session of the Sub-Committee of Experts on the Transport of Dangerous Goods (TDG Sub-Committee), it was decided to introduce a new division 4.1 for polymerizing substances.

2. In 2.4.2.5.1, the definition describes polymerizing substances as "substances which, without stabilization, are liable to undergo a strongly exothermic reaction resulting in the formation of larger molecules or resulting in the formation of polymers under conditions normally encountered in transport."

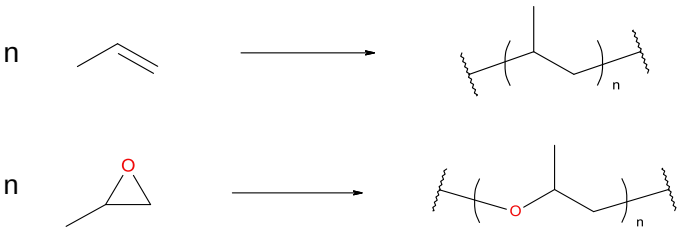
3. However, given that the energy criterion of more than 300 J/g is met, in-depth chemical knowledge is required to understand and assess whether a substance is able to polymerize, rearrange or decompose (and, in the latter case, be a candidate for classification as a self-reactive substance), and to come to the correct conclusion about the classification.

4. Therefore, industry believes it would be helpful to introduce some provisions that are scientifically sound and simple to apply in order to correctly identify substances that should be classified as polymerizing.

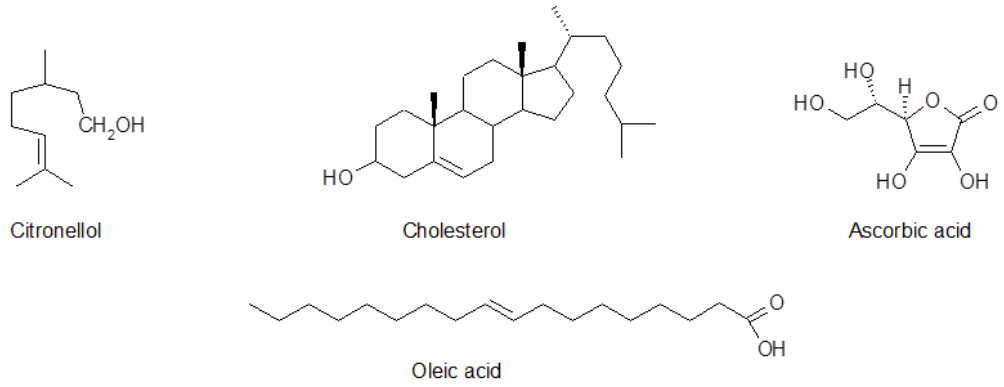
5. Members of the Subcommittee are requested to review this paper and to forward any comments to the CEFIC delegation who intends to submit a formal proposal in this matter for the December session.

Discussion

6. In most chemical textbooks, the ability to polymerize is linked to the existence of unsaturated (i.e. double or triple) bonds or strained rings in the molecule. Thus, polymerization is essentially the formation of a large molecule by addition of small reactive units – the so-called monomers – to the activated end of a growing chain.



7. However, the presence of strained rings or unsaturated bonds by themselves does not constitute that a substance will necessarily polymerize. In fact, many substances with such functional groups will not form large molecules by polymerization. Some examples are shown below:



Citronellol Cholesterol Ascorbic acid

Oleic acid

8. In general, only rather small molecules will polymerize since the formation of chains becomes more unlikely due to steric reasons in larger molecules. As a second effect, the kinetic frequency factor for the chain-building mechanism drops significantly with increasing size of the molecule, and chain interruption reactions becomes more likely.

9. Further, polymerization will not take place in the solid state since a molecule in a crystal lattice will not have the freedom to carry a chain-building mechanism.

10. A practical difficulty is the fact that measurement of energy (for example, by DSC according to 20.3.3.3 of the UN Manual of Tests and Criteria) does not distinguish between contributions due to decomposition or polymerization. In general, decomposition becomes predominant with increasing molecular size.

11. In order to challenge the statements made above, a broad variety of substances in the market which are known to have the potential of polymerization – many of them with individual UN numbers – has been investigated (see table 1).

12. It is found that with increasing size of the molecule the heat of polymerization will drop significantly. This can be explained easily since the energy of the reactive functional groups is released in ratio to the molecular mass.

13. However, the molecular mass in itself is not the optimal criterion because some “heavy” atoms like chlorine, bromine and silicon will substantially increase the molecular weight whereas the molecule remains rather small (see for example Bromopropyne, Vinylbromide, Vinyltrichlorosilane). Therefore, it is suggested to take only the elements C, H, O and N into account as a criterion for the size of the molecule. Thus M(CHON) is the molecular mass counting only the contributions of these elements.

14. A plot of the polymerization energy versus M(CHON) shows nicely the decrease of the maximum energy with increasing size of the molecule. In fact, none of the compounds exhibits a M(CHON) value of 150 g/mol, and the maximum energy approaches the 300 J/g border value (see figure 1)

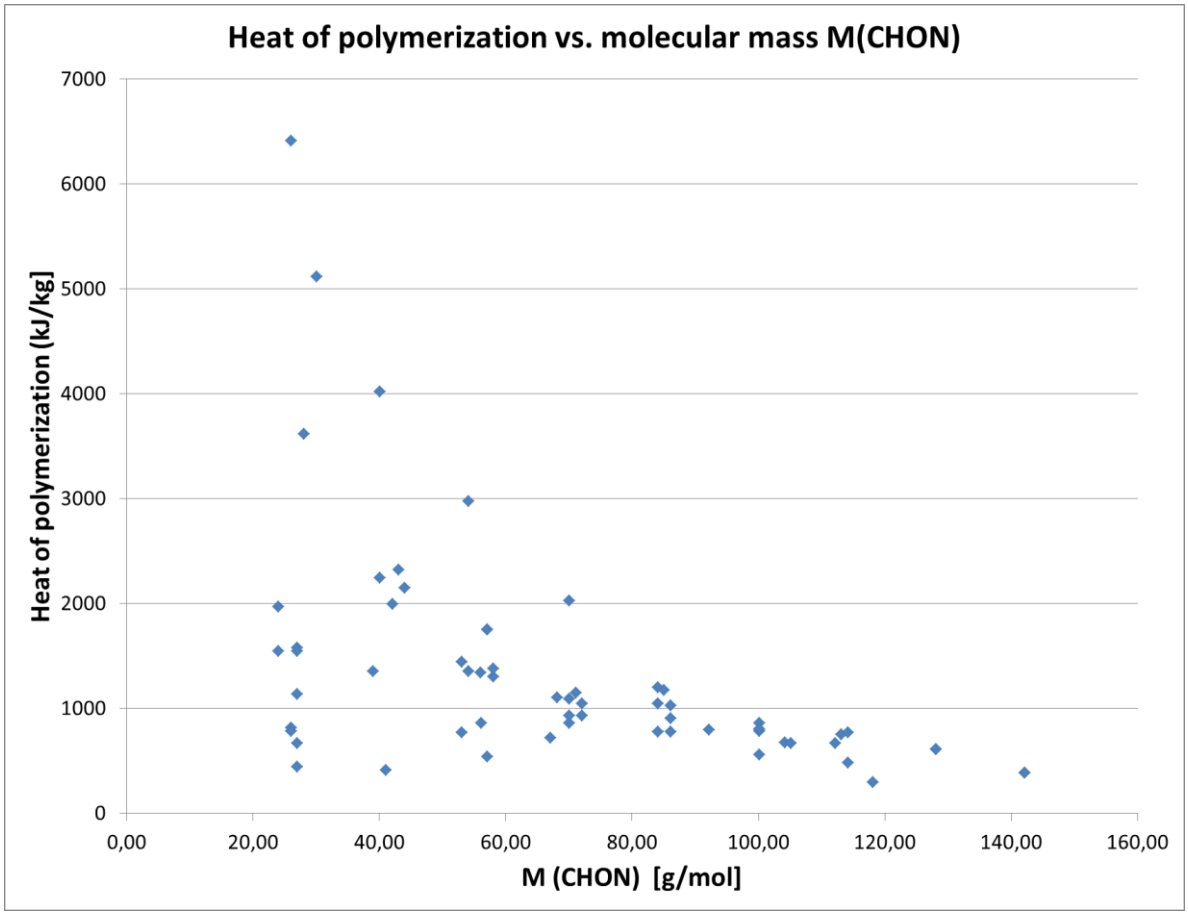


Figure 1: Correlation between energy and molecular mass M(CHON)

Proposal

15. In the UN Manual of Tests and Criteria, appendix 6 (Screening Procedures), insert a chapter 5.2 as follows:

5.2 Substances which may be polymerizing substances (Division 4.1)

The classification procedure for polymerizing substances need not be applied if

(a) the chemical structure of the substance contains no double or triple bonds or strained rings,

(b) or, the compounds contains double or triple bonds or strained rings, but the molecular mass M(CHON) counting only the elements C, H, O and N is more than 150,

(c) The compound is solid with a melting point above (50 °C)

16. Renumber the existing chapters 5.2 to 5.3 and 5.3 to 5.4

Justification

17. This proposal helps to identify substances that fulfill the classification criteria and gives clear cutoff criteria, thus avoiding confusion and unnecessary testing.

		Formula										Molecular mass counting only elements C, H, O and N			
Name	UN Number	C	H	O	N	F	Cl	Br	S	Si	Molecular mass	M(CHON)	Heat of polymerisation (kJ/ mol)	Heat of polymerization (kJ/kg)	
Tetrafluoroethylene	1081	2				4					100,02	24,02	196,8	1967	
Trifluorochloroethylene	1082	2				3	1				116,47	24,02	180,0	1545	estimated from Tetrafluoroethylene
Cyanogenchloride	1589	1			1		1				61,47	26,02	50,0	813	estimated from hydrogen cyanide
Vinylidenchloride	1303	2	2				2				96,94	26,04	75,5	779	Lit.
Acetylene	3374	2	2								26,04	26,04	167,0	6413	SCF calc.
Hydrogen cyanide	1051, 1614	1	1		1						27,03	27,03	42,7	1578	Lit.
Vinylchloride	1086	2	3				1				62,50	27,05	71,0	1136	Lit.
Vinyltrichlorosilane	1305	2	3				3			1	161,49	27,05	71,0	440	estimated from Vinylchloride
Vinylbromide	1085	2	3					1			106,95	27,05	71,0	664	see Vinylchloride
Vinylfluoride	1860	2	3			1					46,05	27,05	71,0	1542	estimate from vinylchloride
Ethene (Ethylene)	1962	2	4								28,05	28,05	101,5	3618	Lit.
Formaldehyde	2209	1	2	1							30,03	30,03	63,0	2098	from literature
3-Bromopropyne	2345	3	3					1			118,96	39,06	161,0	1353	estimated from propyne
Propyne		3	4								40,07	40,07	161,0	4018	SCF calc.
Propadiene	2200	3	4								40,07	40,07	90,0	2246	estimated from propene
Allyltrichlorosilane	1724	3	5				3			1	175,52	41,07	72,5	413	SCF calc.
Propene (Propylene)	1077	3	6								42,08	42,08	84,0	1996	Lit.
Ethyleneimine	1185	2	5		1						43,07	43,07	100,0	2322	estimated from ethyleneoxide
Ethenoxide (Ethylene oxide)	1040	2	4	1							44,05	44,05	94,5	2145	Lit.
Acrylonitrile	1093	3	3		1						53,07	53,07	76,5	1442	Lit.
Chloroprene	1991	4	5				1				88,54	53,09	68,0	768	Lit.
Butadiene	1010	4	6								54,09	54,09	73,0	1350	Lit.
Ethylacetylene	2452	4	6								54,09	54,09	161,0	2976	estimated from propyne
Acroleine	1092	3	4	1							56,07	56,07	75,0	1338	estimated from Acrylic derivatives
Isobuten (Isobutylene)	1055	4	8								56,11	56,11	48,0	855	Lit.
Chloroacetone	1695	3	5	1			1				92,53	57,07	50,0	540	estimated from hydrogen cyanide
Propyleneimine	1921	3	7		1						57,10	57,10	100,0	1751	estimated from ethyleneoxide
Propyleneimine	1919	3	7		1						57,10	57,10	100,0	1751	estimated from ethyleneoxide
Propenoxide (Propylene oxide)	1280	3	6	1							58,08	58,08	75,5	1300	Lit.
Vinylmethylether	1087	3	6	1							58,08	58,08	80,0	1377	estimated from Vinylchloride and Vinylacetate
Allylisothiocyanate	1545	4	5		1				1		99,16	67,09	71,0	716	estimate from vinylchloride
Isoprene	1218	5	8								68,12	68,12	75,0	1101	Lit.
Crotonaldehyde	1143	4	6	1							70,09	70,09	60,0	856	estimated from methacrylic derivatives
Methylvinylketon	1251	4	6	1							70,09	70,09	65,0	927	estimated from methacrylic derivatives
Methacrylaldehyde	2396	4	6	1							70,09	70,09	76,5	1091	estimated from acrylonitrile
Divinylether	1167	4	6	1							70,09	70,09	142,0	2026	estimated from vinylchloride
Acrylamid	2074	3	5	1	1						71,08	71,08	81,5	1147	Lit.
Acrylic acid	2218	3	4	2							72,07	72,07	67,0	930	Lit.
1,2-Butylene-oxide	3022	4	8	1							72,11	72,11	75,5	1047	estimated from propenoxide
Diketene	2521	4	4	2							84,08	84,08	101,0	1201	estimated from ethene
Methylisopropenylketon	1246	5	8	1							84,12	84,12	65,0	773	estimated from methacrylic derivatives
Vinylethylether	1302	5	8	1							84,12	84,12	88,0	1046	estimated from vinylacetate
Acetonecyanhydrine	1541	4	7	1	1						85,11	85,11	75,5	887	estimated from hydrogen cyanide
Acrylic acid methylester	1919	4	6	2							86,09	86,09	78,0	906	Lit.
Vinylacetate	1301	4	6	2							86,09	86,09	88,0	1022	Lit.
Methacrylic acid	2531	4	6	2							86,09	86,09	67,0	778	estimated from acrylic acid
Bicyclo[2.2.1]-hepta-2,5-dien	2251	7	8								92,14	92,14	73,0	792	estimated from butadiene
Methacrylic acid methylester	1247	5	8	2							100,12	100,12	55,5	554	Lit.
Vinylpropionate		5	8	2							100,12	100,12	86,0	859	Lit.
Ethylacrylate	1917	5	8	2							100,12	100,12	78,0	779	estimated from methylacrylate
Vinylisobutylether	1304	6	12	1							100,16	100,16	80,0	799	estimated from vinylacetate
Butylvinylether	2352	6	12	1							100,16	100,16	80,0	799	estimated from vinylacetate
Styrene	2055	8	8								104,16	104,16	70,0	672	Lit.
Vinylpyridine	3073	7	7		1						105,14	105,14	70,0	666	estimated from styrene
Acrolein dimer	2607	6	8	2							112,13	112,13	75,0	669	estimated from acroleine
ε-Caprolactam		6	11	1	1						113,16	113,16	84,9	750	Lit.
Ethylmethacrylate	2277	6	10	2							114,15	114,15	55,0	482	estimated from methylmethacrylate
Vinylbutyrate	2838	6	10	2							114,15	114,15	88,0	771	estimated from vinylacetate
Methylstyrene (vinyltoluene)	2618	9	10								118,18	118,18	35,0	296	Lit.
Butylacrylate	2348	7	12	2							128,17	128,17	78,0	609	estimated from methylacrylate
Isobutylacrylate	2527	7	12	2							128,17	128,17	78,0	609	estimated from methylacrylate
n-Butylmethacrylate	2227	8	14	2							142,20	142,20	55,0	387	estimated from methylmethacrylate
Isobutylmethacrylate	2283	8	14	2							142,20	142,20	55,0	387	estimated from methylmethacrylate

Table 1 Molecular mass and heat of polymerization of known substances