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

Sub-Committee of Experts on the Transport of Dangerous Goods **16 November 2023**

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Item 3 of the provisional agenda
Listing, classification and packing

New special provision and special packing provision of UN 2029

Transmitted by the expert from China

I. Introduction

1. Hydrazine anhydrous (CAS No. 302-01-2) is a widely used raw material. With high combustion heat, it can be used as fuel for rockets and fuel cells, foaming agents, crop insecticides, water treatment agents, etc. UN number 2029 in the Model Regulations is assigned, and the hazard class is Class 8. The subsidiary hazard is Class 3 and/or 6.1.

2. After hydrazine anhydrous based propellants (content ≥ 99 %) have caused many explosion accidents, its hazard classification was examined by the Nanjing University of Science and Technology (NUST). For this purpose, UN test series 1, 3 and 6 have been performed.

3. The test results showed that: (i) In UN test series 1, the results of UN gap test and time/pressure test are both "-" while the result of Koenen test is "+" with the limiting diameter of 3.0 mm; (ii) in test series 3, the results of 3 (a), 3 (b), 3 (c) and 3 (d) are all "-"; (iii) after the sample was packaged in stainless steel tank, test series 6 was carried out and in UN test 6 (a), the test result is "-". In UN test 6 (c), the reaction characteristics of the sample are highly dependent on packaging configurations. Different reactions such as explosion, deflagration and burning of the hydrazine anhydrous may occur under different packaging configurations. The stronger the confinement, the more hazardous the reaction. More details of the test results are presented in the annex to this document.

4. To avoid major changes to the classification of hydrazine anhydrous in the *UN Model Regulations* and significant impact on the existing hydrazine anhydrous industry, China (NUST) submitted a document to the TDG Sub-Committee at the sixtieth session (ST/SG/AC.10/C.3/2022/40). It is proposed to add special provisions for hydrazine anhydrous and its packaging configurations to effectively improve the safety of hydrazine anhydrous during transportation. At that meeting, several delegates asked for more data.

5. At the 2023 IGUS-EPP meeting, the experts from China presented detailed experimental data and video recordings. The Explosives Working Group (EWG) discussed the test data and came to a positive conclusion.

6. China (NUST) submitted an informal document to the TDG Sub-Committee at the 62nd session (UN/SCETDG/62/INF.35). China introduced INF.35 and presented a slideshow and videos to support the paper, which proposed amendments for the entry for hydrazine anhydrous (UN 2029) by adding special provision (SP) 132, special packing provision PP5, and a new special provision. The Explosives Working Group discussed the document. The United Kingdom commented that the special provision looked more like guidance and suggested alternative approaches for drafting. AEISG pointed out that many substances would react this way if packed like this. USA supported adding special packing provision PP5 but did not see the purpose of the new special provision since P001 is assigned to the

entry and already restricts to packaging that prevent confinement, and any other packaging that does not meet P001 would require separate consideration. SAAMI added that the substance is very toxic and caustic, and is packaged like this to prevent release. Cefic noted that other containers are possible. SAAMI responded that some groups use them, but some do not feel that sort may be safe enough to prevent the release of a toxic substance. The EWG supported the addition of SP 132. The TDG Sub-Committee recommended that China reach out to those members who had made suggestions for improvements.

II. Proposal

7. In 3.2 Dangerous Goods List, amend the entry for UN 2029 by adding special provision 132 and special packing provision PP5, as follows (newt text is bold underlined):

UN No.	Name and description	Class	Subsidiary hazard	UN packing group	Special provisions	Limited and excepted quantities		Packagings and IBCs		Portable tanks and bulk containers	
								Packing instruction	Special packing provisions	Instructions	Special provisions
2029	Hydrazine Anhydrous	8	3 6.1	I	**<u>132</u>**	0	E0	P001	**<u>PP5</u>**		

8. In 4.1.4.1 amend special packing provision PP5 to read as follow (new text is underlined):

> “**PP5** For UN <u>Nos.</u> 1204 <u>and 2029</u>, packagings shall be so constructed that explosion is not possible by reason of increased internal pressure. Gas cylinders and gas receptacles shall not be used for these substances.”

Annex

Results of test series 6 (c) for hydrazine anhydrous under different packaging conditions

Submitted by: CHINA Date: 1 April, 2022

1. Preliminary 6 (c) test on hydrazine anhydrous

Test condition：20 L cylindrical stainless steel storage tank. Pressure resistance of the tank shell is 1 MPa. Kerosene was used as fuel.

Figure 1: 20 L cylindrical stainless steel storage tank in the 6 (c) test.

Figure 2: Fragments of the tank after the test.

Test result : mass explosion occurred, and the storage tank was completely shattered.

Remark : This test was designed to simulate an accident scene. Considering that hydrazine anhydrous is classified as UN 2029 (Class 8), no explosion was anticipated. Therefore, shock wave measurement system and high-speed video were not deployed during the test. Based on this test results, the second repetition test was designed.

2. Second 6 (c) test on hydrazine anhydrous

Test condition：20 L cylindrical stainless steel storage tank. Pressure resistance of tank shell is 1 MPa. Kerosene was used as fuel.

Figure 3: 20 L cylindrical stainless steel storage tank in the 6 (c) test.

Figure 4: Fragments of the tank after the test.

0 ms 100 ms

500 ms 1000 ms

1500 ms

Figure 5: Screen shots from high-speed video during the test.

Results of the shock wave overpressure in the air measured during the second test.

Table 1 below shows the peak of shock wave overpressure in the air when the sample exploded.

Table 1: the peak of shock wave overpressure

Sample	Test line	Shock wave overpressure (kPa)							
		5 m	7 m	9 m	11 m	14 m	16 m	18 m	21 m
hydrazine anhydrous packaged in 20 L cylindrical stainless steel tank	1	320.72	172.05	91.86	72.51	50.11	41.48	30.42	25.95
	2	339.60	148.89	96.38	65.63	43.47	32.33	25.63	21.14

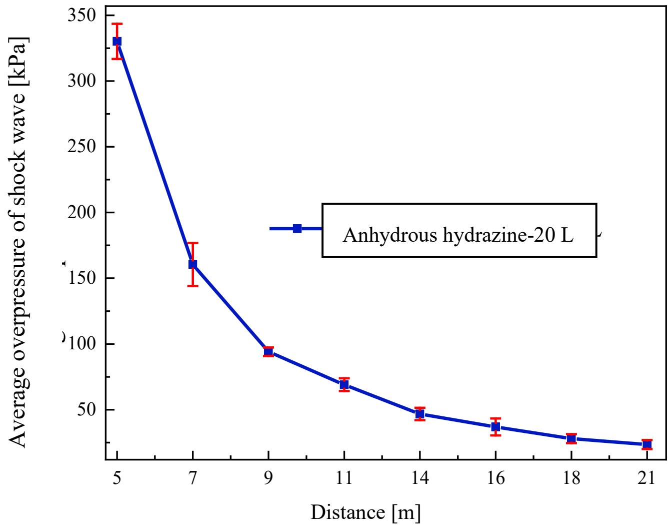

Figure 6: The relationship between shock wave overpressure and distance

Take $\overline{R} = R/\sqrt[3]{w}$ as abscissa, and shock wave overpressure as ordinate. Using the explosion similarity law, the fitted curve and the equation of the fitted curve can be obtained by fitting the shock wave over pressure to the distance.

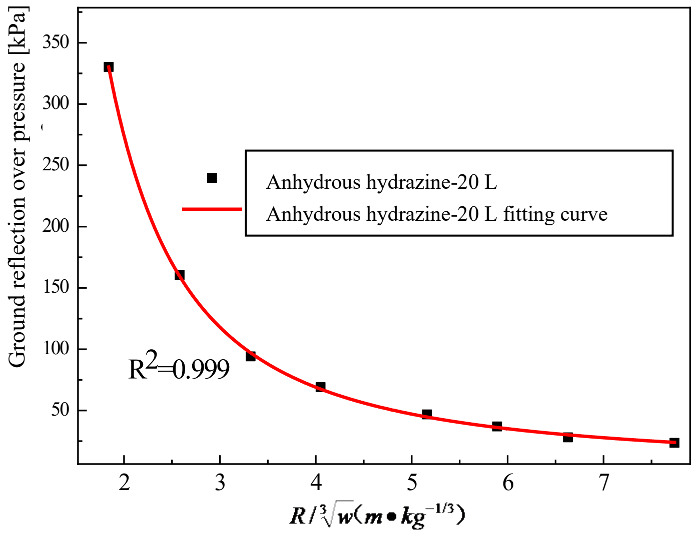

Figure 7: Relationship between shock wave overpressure and $\overline{R}$

Fitting equation：

$$p = 129.09 \times \sqrt[3]{w}/R + 378.07 \times \left(\sqrt[3]{w}/R\right)^2 + 1107.75 \times \left(\sqrt[3]{w}/R\right)^3$$

Substitute the shock wave overpressure of the sample into the fitting equation of TNT ($P = 0.109 \times \sqrt[3]{w}/R + 0.56 \times \left(\sqrt[3]{w}/R\right)^2 + 1.98 \times \left(\sqrt[3]{w}/R\right)^3$), Table 2 shows the TNT equivalent of the sample explosion.

Table 2: TNT equivalent of hydrazine anhydrous explosion

Sample	TNT equivalent [kg]									TNT equivalent
	5 m	7 m	9 m	11 m	14 m	16 m	18 m	21 m	Average	
hydrazine anhydrous packaged in 20 L cylindrical stainless steel tank	10.86	11.57	11.56	13.25	14.68	14.69	12.85	14.79	13.03	0.72

Test result: mass explosion occurred, storage tank was completely shattered, and the evident shock wave overpressure was measured.

3. Third 6 (c) test on hydrazine anhydrous

Test condition：120 L cylindrical stainless steel storage tank. Pressure resistance of tank shell is 0.33 MPa. Kerosene was used as fuel.

Figure 8: Hydrazine anhydrous packaged in 120 L cylindrical stainless steel storage tank.

0 ms

100 ms

500 ms

1000 ms

1500 ms 2000 ms

Figure 9: Screen shots from high-speed video during the third test.

Figure 10: The witness plate and tank after test.

Results of shock wave overpressure measured during test.

Table 3 shows the peak of shock wave overpressure when the sample exploded.

Table 3: The peak of shock wave overpressure

Sample	Test line	Shock wave overpressure [kPa]							
		5 m	7 m	9 m	11 m	14 m	16 m	18 m	21 m
hydrazine anhydrous packaged in 120 L cylindrical stainless steel tank	1	10.382	8.390	5.755	4.511	3.264	2.437	1.867	1.600
	2	9.242	7.801	6.357	4.165	3.765	2.915	2.760	0.729

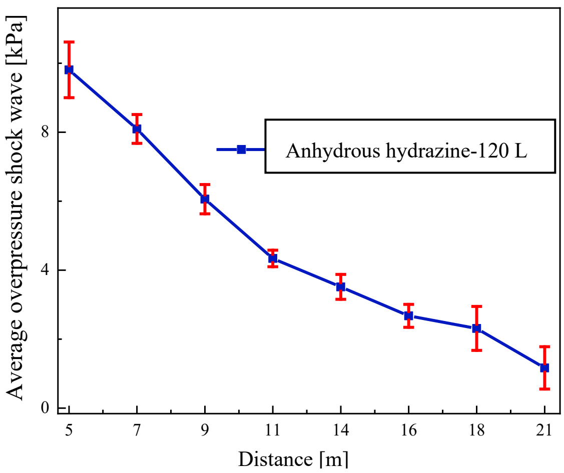

Figure 11: Relationship between shockwave overpressure and distance

Take $\overline{R} = R/\sqrt[3]{w}$ as abscissa, and shock wave over pressure as ordinate. Using the explosion similarity law, the fitted curve and the equation of the fitted curve can be obtained by fitting the shock wave over pressure with the distance.

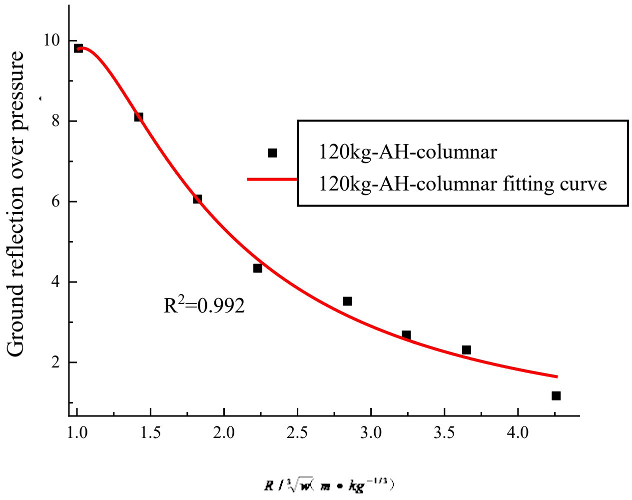

Figure 12: Relationship between shock wave overpressure and $\overline{R}$

Fitting equation：

$$P = 1.43 \times \sqrt[3]{w}/R + 28.54 \times \left(\sqrt[3]{w}/R\right)^2 - 20.20 \times \left(\sqrt[3]{w}/R\right)^3$$

Substitute the shock wave overpressure of sample into fitting the equation of TNT ($P = 0.109 \times \sqrt[3]{w}/R + 0.56 \times \left(\sqrt[3]{w}/R\right)^2 + 1.98 \times \left(\sqrt[3]{w}/R\right)^3$), Table 2 shows the TNT equivalent of sample explosion.

Table 4: TNT equivalent of hydrazine anhydrous explosion

Sample	TNT equivalent /kg									TNT equivalent
	5 m	7 m	9 m	11 m	14 m	16 m	18 m	21 m	average	
hydrazine anhydrous packaged in 120 L cylindrical stainless steel tank	0.034	0.059	0.063	0.049	0.059	0.044	0.041	0.011	0.045	0.00038

Test result: during the test, the tank burst and the hydrazine anhydrous burnt stably. No mass explosion occurred. After test, no damage or perforation of the witness screens was observed, and no shock wave overpressure was measured in the air.

Conclusion

4. The above test results have shown that the packaging configurations have a significant impact on the hazardous reaction of hydrazine anhydrous. In over-confined packagings, it will react violently and explode in a fire. To avoid major changes to the classification of hydrazine anhydrous in the *UN Model Regulations* and significant impact on the existing hydrazine anhydrous industry, it is proposed to add special provisions on hydrazine anhydrous and its packaging configurations to effectively improve the safety of hydrazine anhydrous during transportation.