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|  |  | **UN/SCETDG/48/INF.22** |

**Committee of Experts on the Transport of Dangerous Goods
and on the Globally Harmonized System of Classification
and Labelling of Chemicals 18 November 2015**

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| **Sub-Committee of Experts on the Transport of Dangerous Goods**  |  |
| **Forty-eighth session** |  |
| Geneva, 30 November – 9 December 2015Item 2 (c) of the provisional agenda**Explosives and related matters: review of tests in parts I and II of the Manual of Tests and Criteria** |  |

On the use of the minimum burning pressure test as a replacement for Tests 8 (c) and 8 (d)

Transmitted by the expert from Spain

Introduction

1. The expert from Canada has presented the document ST/SG/AC.10/C.3/2015/41, proposing:

“To amend Test Series 8 in order to replace the current Tests 8 (c) (Section 18.6.1 Koenen Test) and 8 (d) (Section 18.7.1 Vented Pipe Test and Section 18.7.2 Modified Vented Pipe Test) with the CERL MBP Test described below in the annex. It is further proposed that inclusion in the UN 3375 and Division 5.1 be restricted to those products having a MBP above 5.6 MPa (800 psig).”

2. The expert from Spain does not consider this proposal appropriate.

Background

3. For many years, the experts of the Sub-Committee of Transport of Dangerous Goods have submitted and have worked on a huge number of INF’s and working documents in relation to the classification, transport approval in portable tanks and tests of “ANEs”; this included the establishment and development of the test Series 8. This process was carried out following a very meticulous methodology, full of analysis, tests and deliberations.

4. Such effort of the experts of the Sub-Committee of Transport of Dangerous Goods had a comprehensive result: the creation of a new entry (ONU 3375), the establishment of the special provision SP 309 and the inclusion in the Manual of Test and Criteria of a new test Series 8.

5. The Series 8 Test consists of 4 tests:

* 8 (a), 8 (b) y 8 (c), for the classification of ANEs -with formulations within the SP 309 parameters- as UN 3375
* 8 (d) test, both, (i) -VPT- and (ii) -MVPT-, which are not for classification, but to state if an ANEs is suitable, or not, for its transport in portable tanks.

6. Even though the technical rigor and validity of the above mentioned approach and tests is undeniable, dissatisfaction with the Vented Pipe Test 8 (d) and Koenen test 8 (c) has been expressed in several occasions.

7. During the biennium 2013-2014 new amendments to Series 8 Tests were accomplished, especially to tests 8 (d) (ST/SG/AC.10/42/Add.2).

8. At the thirty-seventh session of the Sub-Committee of Experts on the Transport of Dangerous Goods, the expert from Canada proposed *that the Working Group considers the potential merit of including the MBP test as an alternative to the current 8(d) test. For example, as an alternative to the 8(d) test, UN 3375 could be restricted to those products with MBP values above 5.6 MPa (800 psig)* (informal document INF.41 (37th session)).

9. Informal document INF.41 (37th session), transmitted by the expert from Canada, did not provide a sufficiently detailed description of the tested compositions and was focused mainly on comparing some cartridge emulsions with some bulk ones.

10. The Canadian proposal was discussed by the Working Group on Explosives, but without reaching a conclusion. Many members offered to perform some tests to help with the further evaluation of the MBP test. The Working Group noted *that it is a basic principle that when evaluating alternative tests, comparability with existing tests is required* (informal document INF.73 (37th session)).

Considerations

11. The validity of the Minimum Burning Pressure test as a replacement for the current Tests 8(c) and 8 (d) presented in proposal ST/SG/AC.10/C.3/2015/41 is unclear and, overall, inadequate:

* Due to its own approach, the MBP test is not an adequate test neither for ANEs classification below UN 3375 nor for its transport approval in portable tanks. The MBP test allows the risk which may occur during a pumping operation, to be evaluated if a hot spot appears in the pump. Whereas Koenen test and vented pipe test deal with a thermal explosion or cook-off phenomenon which is a consequence of a reaction runaway in a chemical system undergoing exothermic reaction. The condition involves the near simultaneous heating of an entire inventory followed by a rapid reaction. Minimum burning pressure test is related with a deflagration phenomenon, which occurs when there is an intense localized internal thermal ignition (hot spot) under pressures sufficiently high to support combustion.
* The attached report shows a clear relationship between modified vented pipe test and Koenen test, however no relationships between MBPT and Koenen tests, and MBPT and MVPT were found. Experimental data clearly support the above statement (Annex: Maxam's technical report: Performance of Minimum Burning Pressure Test (CANMET Procedure) on Ammonium Nitrate Emulsions and Suspensions (ANEs)).

12. The comparability between the present tests, accepted and validated by practice, and any new tests is basic. ANEs classified according to the present tests should maintain their present classification with any new test proposed.

Proposal

13. The expert from Spain does not support the minimum burning pressure test as replacement or alternative for Tests 8 (c) and 8 (d), because it does not provide the proper information about the hazard considered and it has been shown that MBP outcomes have no relation to those from Koenen and VPT tests.

Performance

of

Minimum Burning Pressure Test (CANMET Procedure)

on

Ammonium Nitrate Emulsions and Suspensions (ANEs)

MAXAM

November 2015

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**0. SUMMARY AND CONCLUSIONS**

The minimum burning pressure test (MBPT) has been applied to a series of ammonium nitrate matrices, both emulsions and suspensions, in accordance with the methodology developed by CANMET. The substances tested have been chosen to cover a wide range of compositions with the aim of assessing how useful the test is to establish whether an ammonium nitrate emulsion, suspension or gel, intermediate for blasting explosives (ANE), can be assigned to Division 5.1 (UN 3375) and the suitability of the substance for its transport in tanks.

The chosen compositions are those already used in a previous study on the modified vented pipe test (MVPT), whose results were reported in document UN/SCETDG/25/INF.74. Koenen test results for the same compositions were also reported in the document. This way, the possibility of comparing results of the three tests was achieved. So, apart from evaluating the MBP results as a function of the components of the ANE candidates, the relationships between the three tests were established.

Whereas a clear relationship between modified vented pipe test and Koenen tests was found, no relationships between MBPT and Koenen test, and MBPT and MVPT were observed.

On the other hand, the MBP results as a function of the different components of the tested substance showed a remarkable contrary pattern to Koenen test and MVPT results. The presence of sodium nitrate in the substance causes a decrease in the MBP (more severe result), contrary to the Koenen test and MVPT results, where a decrease in the limiting diameters (less severe result) was observed. On the other hand, no different MBP results were observed between substances containing sodium nitrate or sodium perchlorate, whereas the substitution of sodium nitrate by sodium perchlorate lead to higher limiting diameters in Koenen test and MVPT.

From the results obtained in this study, we can conclude that MBP test is not an alternative test to Koenen and modified vented pipe tests. This conclusion is not surprising if the phenomena associated with these tests are taking into account.

Whereas Koenen test and vented pipe test deal with a thermal explosion or cook-off phenomenon, which is a consequence of a reaction runaway in a chemical system undergoing exothermic reaction. The condition involves the near simultaneous heating of an entire inventory followed by a rapid reaction. Minimum burning pressure test is related with a deflagration phenomenon which occurs when there is an intense localized internal thermal ignition (hot spot) under pressures sufficiently high to support combustion.

**1. INTRODUCTION**

It is well known that water-based explosives or precursors can sustain combustion only when the ambient pressure is held above some threshold value which is denominated minimum burning pressure (MBP). The pumping operations are frequent on manufacturing and use of these energetic materials, so the product can be undergone to high pressures. Accordingly, knowing the MBP of the involved material is very useful in order to evaluate the risk on the pumping operations. Therefore, substantial efforts have been carried out to have a suitable test to determine the minimum burning pressure of a substance.

At the thirty-seventh session of the Sub-Committee of Experts on the Transport of Dangerous Goods, the expert from Canada presented the document UN/SCETDG/37/INF.41 ‘On the use of the minimum burning pressure test as an alternative Series 8 Test’ **(1)**. The document revealed some comparative data between bulk and cartridge emulsions, although the detailed compositions were not described, concluding that the water content of the substance had an important effect on the test results. That document included a proposal saying:

*That the Working Group considers the potential merit of including the MBP test as an alternative to the current 8(d) test. For example, as an alternative to the 8(d) test, UN 3375 could be restricted to those products with MBP values above 5.6 MPa (800 psig)*.

During the discussion of this document at the Working Group on Explosives **(2),** comparative results between the proposed test as alternative (MBPT) and current 8(d) tests were not given. The working group noted that it was a basic principle that when evaluating alternative tests, comparability with existing tests was required. The conclusion of the working group was:

*The working group agreed that the MBP test might be a good way forward in evaluating the hazards associated with tank transportation of ANEs. Many members offered to perform some tests to help with the further evaluation of the MBP test*.

Due to the lack of existing data to perform a comparative study between different tests, Maxam undertook a project to determine the MBP values for all emulsions and suspensions used on the development of 8(d) (ii) Test, the modified vent pipe test **(3).** The results of limiting vent diameter (LD) of the modified vent pipe test and the Koenen test for 15 bulk emulsions and 7 bulk suspensions with diverse componentswere describedat the documentUN/SCETDG/25/INF.74 **(3)**.

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In order to obtain conclusive data determining the minimum burning pressure for the different considered ANEs, the same equipment and procedure, established by the CANMET, has been used. To this end, several conversations were held with technical staff of the site, and also comparative tests were carried out, verifying similar results.

The possible correlations between the three tests have been studied with the results obtained in the MBP measures and those corresponding to the Koenen test and modified vented pipe test, already described at the document UN/SCETDG/25/INF.74 **(3)**.

**2. EXPERIMENTAL**

**2.1. Apparatus and procedure**

The MBP for every sample was determined using the methodology developed by CANMET **(4, 5)**. Measurements were performed in a 4 L pressure vessel (Autoclave Engineers, 4 Liter EZE-Seal General Arrangement, model 401A-9344) with no venting during testing. Purging and pressurizing were performed by using high pressure nitrogen cylinders.

|  |  |
| --- | --- |
| P0006612 | Muestra1 |
| Muestra2 |
| **Figure 1. Pressure vessel** | **Figure 2. Test cell** |

The sample was introduced into a cylindrical stainless steel cell which was placed horizontally. The steel tube had an inner diameter of 13.2 mm and a length of 70 mm. The tube had a slit machined along the top portion of the tube with a width of 3 mm and a length of 53 mm.

The sample was ignited at room temperature, using a straight length of nichrome wire (Thyssenkrupp Ni/Cr 60/15) having a diameter of 0.5 mm, a length of 50 mm and a nominal resistance of 5.731 Ω.m-1. When the pressure vessel was set to the desired initial pressure, a constant current of 10 A was supplied to the hot wire. This current was provided by a TTI DC power supply unit, model TSX 1820. Usually, the wire melted before 10 s. In cases in which the wire did not come to melt, the power supply unit was switched off after 20 seconds.

The pressure in the vessel was monitored using a Setra pressure transmitter model C206 (0-20.68 MPa) and the data acquisition system consisted of a Testo datalogger model 175-S1, which was connected to a PC by a RS232 interface.

The procedure to perform the MBP measurements was based on classifying the outcomes as “go“ or “no-go”, considering a “go” outcome when at least a 70 % in weight of the sample was consumed. If the result was a “go”, the initial pressure was lowered for the following test. If the result was a “no-go”, the initial pressure was increased. This process was repeated several times until the MBP was got with the required accuracy.

**2.2. Tested substances**

With the objective of assessing whether this test can distinguish between different substances from the point of view of risk during transport, a series of compositions have been chosen that cover a wide range of emulsions, as well as suspensions. These compositions were once used to evaluate the modified vented pipe test, as well as to analyse its correlation with the Koenen Test **(3)**.

Twelve different emulsions were tested that included different water content, the presence of sodium perchlorate and sodium nitrate, together with different types and percentages of emulsifiers (PIBSA and SMO types).

With the same criteria in the compositions, seven suspension formulations have been chosen. Compositions with sodium perchlorate, methylamine nitrate, and hexamine nitrate were included, as well as one without any of those components.

The specified compositions of the substances, used in this study, are shown in Table 1. In all cases the viscosity was found to be between 30 and 60 Pa⋅s.

**Table 1. Substances tested**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Emulsions** | **EM1** | **EM2** | **EM3** | **EM4** | **EM5** | **EM6** | **EM10** | **EM11** | **EM12** | **EM13** | **EM14** | **EM15** |
| Ammonium nitrate | 76.0 | 82.1 | 74.9 | 67.7 | 66.0 | 84.0 | 72.0 | 74.0 | 74.0 | 76.0 | 76.0 | 76.0 |
| Sodium nitrate | - | - | - | 12.2 | - | - | 12.0 | - | - | - | - | - |
| Sodium perchlorate | - | - |  9.7 | - | 10.0 | - | - | 10.0 | 10.0 | - | - | - |
| Water | 17.0 | 12.3 |  9.0 | 14.1 | 17.0 |  9.0 |  9.0 |  9.0 |  9.0 | 17.0 | 17.0 | 17.0 |
| Paraffin oil |  5.6 |  4.2 |  3.7 |  4.8 |  5.6 |  5.6 |  5.6 |  5.0 |  5.6 |  4.2 |  6.6 |  4.2 |
| PIBSA emulsifier |  1.4 |  1.4 |  2.7 |  1.2 |  1.4 |  1.4 |  1.4 |  2.0 | 1.4 |  2.8 |  0.4 | - |
| SMO emulsifier | - | - | - | - | - | - | - | - | - | - | - |  2.8 |
| **Suspensions** | **SP1** | **SP2** | **SP3** | **SP4** | **SP5** | **SP6** | **SP7** |  |  |  |  |  |
| Ammonium nitrate | 62.3 | 55.0 | 67.4 | 71.4 | 66.4 | 68.4 | 56.4 |  |  |  |  |  |
| Sodium nitrate | - |  8.0 | - | - | - | - | 15.0 |  |  |  |  |  |
| Sodium perchlorate | 11.0 |  8.0 | - | - |  8.0 | - | - |  |  |  |  |  |
| Methylamine nitrate | - | - | 15.0 | - | - | 10.0 | - |  |  |  |  |  |
| Hexamine nitrate | - | - | - | 14.0 |  7.0 | - | - |  |  |  |  |  |
| Water | 13.0 | 14.0 | 12.0 | 14.0 | 12.0 | 13.0 | 15.0 |  |  |  |  |  |
| Glycol | 13.0 | 14.0 |  5.0 | - |  6.0 |  8.0 | 13.0 |  |  |  |  |  |
| Thickener |  0.7 |  1.0 |  0.6 |  0.6 |  0.6 |  0.6 |  0.6 |  |  |  |  |  |

**3. RESULTS**

The results obtained of minimum burning pressure measurements for different emulsions and suspensions are shown in Table 2. The initial pressure of the lowest “go” event is shown in the column “go”, and the initial pressure of the highest “no-go” event, but lower than above “go” event is shown in the column “no-go”. The MBP was determined as the mean of both pressures.

**Table 2. MBP results**

|  |  |  |
| --- | --- | --- |
| **Compositions** | **Pressure (MPa)** | **MBP****(MPa)** |
| **go** | **no-go** |
| **EM1** AN 76.0%, W 17.0%, PO 5.6%, PIBSA 1.4% | 12.20 | 11.83 | 12.02 |
| **EM2** AN 82.1%, W 12.3%, PO 4.2%, PIBSA 1.4% |  6.93 |  6.37 |  6.65 |
| **EM3** AN 74.9%, SP 9.7%,W 9.0%, PO 3.7%, PIBSA 2.7% |  3.28 |  3.00 |  3.14 |
| **EM4** AN 67.7%, SN 12.2%, W 14.1%, PO 4.8%, PIBSA 1.2% |  4.77 |  4.70 |  4.74 |
| **EM5** AN 66.0%, SP 10.0%, W 17.0%, PO 5.6%, PIBSA 1.4% |  5.45 |  5.35 |  5.40 |
| **EM6** AN 84.0%, Water 9.0%, PO 5.6%, PIBSA 1.4% |  3.44 |  3.04 |  3.24 |
| **EM10** AN 72.0%, SN 12.0%,W 9.0%, PO 5.6%, PIBSA 1.4% |  2.92 |  2.58 |  2.75 |
| **EM11** AN 74.0%, SP 10.0%, Water 9.0%, PO 5.0%, PIBSA 2.0% |  3.42 |  3.05 |  3.24 |
| **EM12** AN 74.0%, SP 10.0%, Water 9.0%, PO 5.6%, PIBSA 1.4% |  2.76 |  2.56 |  2.66 |
| **EM13** AN 76.0%, W 17.0%, PO 4.2%, PIBSA 2.8% | 14.61 | 13.82 | 14.22 |
| **EM14** AN 76.0%, W 17.0%, PO 6.6%, PIBSA 0.4% | 12.91 | 12.70 | 12.81 |
| **EM15** AN 76.0%, W 17.0%, PO 4.2%, SMO 2.8% | 11.80 | 11.50 | 11.65 |
| **SP1** AN 62.3%, SP 11.0%, W 13.0%, G 13.0%, T 0.7% |  5.29 |  5.05 |  5.17 |
| **SP2** AN 55.0%, SP 8.0%, SN 8.0%, W 14.0%, G 14.0%, T 1.0% |  6.41 |  6.11 |  6.26 |
| **SP3** AN 67.4%, MAN 15.0%, W 12.0%, G 5.0%, T 0.6% |  9.06 |  8.74 |  8.90 |
| **SP4** AN 71.4%, HN 14.0%, W 14.0%, T 0.6% |  1.55 |  1.53 |  1.54 |
| **SP5** AN 66.4%, SP 8.0%, HN 7.0%, W 12.0%, G 6.0%, T 0.6% |  0.70 |  0.63 |  0.67 |
| **SP6** AN 68.4%, MAN 10.0%, W 13.0%, G 8.0%, T 0.6% |  7.90 |  7.52 |  7.71 |
| **SP7** AN 56.4%, SN 15.0%, W 15.0%, G 13.0%, T 0.6% |  7.18 |  7.09 |  7.14 |

**NOTA:** AN: ammonium nitrate, SP: sodium perchlorate, SN: sodium nitrate, W: water, PO: paraffin oil, PIBSA: PIBSA emulsifier, SMO: sorbitan monoleate, HN: hexamine nitrate, MAN: methylamine nitrate, G: glycol, T: thickener

**4. DISCUSSION**

Table 3 shows the values of the limiting diameter obtained in the Koenen test and the modified vented pipe test, from a previous study **(3)**, and the minimum burning pressure values obtained in the present study for a series of emulsions and suspensions. Limiting diameter corresponds to the maximum venting diameter at which an explosion occurred.

**Table 3. Limiting diameters (LD) for Koenen and modified vented pipe tests (3) and minimum burning pressure (MBP) for the different emulsions and suspensions prepared.**

|  |  |  |  |
| --- | --- | --- | --- |
| **Compositions** | Koenen LD**(mm)** | MVPT LD**(mm)** | **MBP****(MPa)** |
| **EM3** AN 74.9%, SP 9.7%, W 9.0%, PO 3.7%, PIBSA 2.7% |  1.50 | ≥100 |  3.14 |
| **EM11** AN 74.0%, SP 10.0%, W 9.0%, PO 5.0%, PIBSA 2.0% |  1.50 |  85 |  3.24 |
| **EM12** AN 74.0%, SP 10.0%, W 9.0%, PO 5.6%, PIBSA 1.4% |  1.50 |  65 |  2.66 |
| **EM5** AN 66.0%, SP 10.0%, W 17.0%, PO 5.6%, PIBSA 1.4% |  1.00 |  65 |  5.40 |
| **EM6** AN 84.0%, W 9.0%, PO 5.6%, PIBSA 1.4% |  1.25 |  90 |  3.24 |
| **EM2** AN 82.1%, W 12.3%, PO 4.2%, PIBSA 1.4% |  1.75 |  80 |  6.65 |
| **EM1** AN 76.0%, W 17.0%, PO 5.6%, PIBSA 1.4% |  1.50 |  65 | 12.02 |
| **EM13** AN 76.0%, W 17.0%, PO4.2%, PIBSA 2.8% |  1.50 |  75 | 14.22 |
| **EM15** AN 76.0%, W 17.0%, PO 4.2%, SMO 2.8% |  1.50 |  65 | 11.65 |
| **EM14** AN 76.0%, W 17.0%, PO6.6%, PIBSA 0.4% | < 0.75 | <30 | 12.81 |
| **EM10** AN 72.0%, SN 12.0%, W 9.0%, PO 5.6%, PIBSA 1.4% |  1.00 |  65 |  2.75 |
| **EM4** AN 67.7%, SN 12.2%, W 14.1%, PO 4.8%, PIBSA 1.2% | < 0.75 |  30 |  4.74 |
| **SP4** AN 71.4%, HN 14.0%, W 14.0%, T 0.6% |  1.50 |  70 |  1.54 |
| **SP5** AN 66.4%, SP 8.0%, HN 7.0%, W 12.0%, G 6.0 %T 0.6% |  1.25 |  45 |  0.67 |
| **SP3** AN 67.4%, MAN 15.0%, W 12.0%, G 5.0%, T 0.6% |  1.00 |  45 |  8.90 |
| **SP6** AN 68.4%, MAN 10.0%, W 13.0%, G 8.0%, T 0.6% | <0.75 | <30 |  7.71 |
| **SP1** AN 62.3%, SP 11.0%,W 13.0%, G 13.0%, T 0.7% |  0.75 |  30 |  5.17 |
| **SP2** AN 55.0%, SP 8.0%, SN 8.0%, W 14.0%, G 14.0%, T 1.0% |  1.00 |  - |  6.26 |
| **SP7** AN 56.4%, SN 15.0%, W 15.0%, G 13.0%, T 0.6% | <0.75 | <30 |  7.14 |

**4.1. Influence of water content**

To analyse the influence of water on the result of the test, we opted to study this influence in case of emulsions as these permit a substantial modification in the water and ammonium nitrate content, maintaining the physical-chemical state (structure and viscosity) of the emulsions unaltered. These changes made in suspensions would lead to a substantial change in the solid/liquid phase relation that would change their structure. AN emulsions EM1, EM2 and EM6 and AN/SN emulsions EM4 and EM10 were included in this analysis.

Figure 3 shows the minimum burning pressures versus the water content for both group of emulsions analysed. Here a clear dependence can be seen, the MBP value decrease as the water content is reduced. These results agree with whose reporter in document UN/SCETDG/37/INF.41 **(1)**, where a figure with similar pattern is shown.



**Figure 3. Minimum Burning Pressure, MBP, as a function of water content for three AN emulsions (circles) and two AN/SN emulsions (triangles).**

This performance seems logical and occurs generally in any sensitivity test for energy materials, regardless of the applied stimulus.

**4.2. Influence of sodium perchlorate**

Analysing the obtained results of MBP, there is clearly a decrease by replacing part of the ammonium nitrate by sodium perchlorate. So while the EM1 and EM6 emulsions present values of 12.02 and 3.24 MPa, respectively, emulsions EM5 and EM12 present 5.40 and 2.66, respectively. It is noted that this influence is most significant with higher water content. Meanwhile for a 17.0% of water, the reduction is 55%, for a water content of the 9.0% reduction is 18%.

 Comparing the limiting diameter (LD) values for the Koenen and MVP tests, as shown in table 3, for the same emulsions, we can see that the replacement of 10% ammonium nitrate by sodium perchlorate does not increase the limiting diameter; it means that the substitution does not lead to more severe results in the Koenen and MVP tests.

**4.3. Influence of sodium nitrate**

To determine the influence of sodium nitrate content at the minimum burning pressure, we only need to analyse Figure 3, where it can be observed that for medium or high water contents, the AN/SN emulsions show MBP values significantly lower than the emulsions containing only ammonium nitrate as the sole oxidant. This result is also described at the UN/SCETDG/37/INF.41 document **(1)**. On the other hand, comparing the EM12 and EM10 emulsions, with similar values of MBP, could be deduced that the influences of sodium nitrate and sodium perchlorate are similar, at least in the studied experimental range.

The obtained results by studying the influence of sodium nitrate content on the MBP of emulsions show a contrary behaviour to those described for the Koenen and MVP tests **(3).** So, taking into account that the difference between EM10 and EM6 emulsions is that a 12.0 % of the ammonium nitrate was substituted for sodium nitrate, it was surprising how the EM6 AN emulsion presents a MVPT LD of 90 mm, while for the EM10 AN/SN emulsion MVPT LD decreases to 65 mm. In the case of the Koenen test, the LD is 1.25 mm for the EM6 AN emulsion and 1.00 mm for the EM10 AN/SN emulsion. That means the replacement of ammonium nitrate by sodium nitrate leads to less severe results for the Koenen test and the MVPT, just the reverse behaviour as the outcome obtained with the minimum burning pressure test.

**4.4. Influence of amine nitrates**

Considering the amine nitrates as fuels, the tested suspensions can be classified in three groups: those containing hexamine nitrate (SP4 and SP5), those containing methylamine nitrate (SP3 and SP6), and those containing glycol as the only fuel. Analysing the MBP obtained values, it could be said that the highest values (7.71-8.90 MPa) belong to the suspensions with methylamine nitrate, the intermediate values (5.17-7.14 MPa) belong to the suspensions with glycol only, and finally, the lowest values (0.67-1.54) belong to the suspensions with hexamine nitrate.

In this case, as most of the factors studied, it could be said that the behaviour of these substances in the MBP test is completely different to that observed in the Koenen test and the modified vented pipe test. If you compare the SP3 and SP5 suspensions that have very similar results in the Koenen (1.00 and 1.25 mm) and MVP tests (45 mm and 45 mm), it can be said that while the SP3 suspension presents a MBP of 8.90 MPa, the SP5 suspension presents a value of 0.67 MPa.

**4.5. Influence of the emulsion stability**

In a previous study on the modified vented pipe test **(3)**, it was observed that the emulsion stability had a remarkable influence on the test outcome. The greater the emulsion stability was, the greater was the limiting diameter obtained. Varying the emulsifier content, it was observed that the greater was the content, the higher was the limiting diameter obtained. It was also noted that the emulsions prepared with a PIBSA emulsifier (polymeric emulsifier), showed greater LD values than those prepared with sorbitan monooleate (low molar mass emulsifier).

However, an influence of the emulsion stability is not appreciated in the case of the MBP test. So, EM3, EM11 and EM12 emulsions, that have decreasing emulsifier contents, show very similar MBPs, 3.24, 3.14 and 2.66 MPa, respectively; while their LD are completely different; ≥100, 85 and 65 mm, respectively. Same behaviour can be observed for one salt EM13 and EM14 emulsions, presenting MBP of 14.22 and 12.81, respectively, and MVPT limiting diameters of 75 and < 30 mm, respectively. The emulsions EM13 (PIBSA) and EM15 (SMO) present MBPs of 14.22 and 11.65 mm, and MVPT limiting diameters of 75 and 65 mm, respectively. That is to say, SMO emulsion showed a less severe MVPT outcome and a more severe MBPT outcome than PIBSA emulsion.

 **4.6. Relationships between MBPT, Koenen and MVPT Test**

 The possible relationship between the limiting diameters of MVP and Koenen tests had been analysed in a previous report **(3)**. Figure 4 shows the MVPT limiting diameter versus the Koenen test limiting diameter for different emulsions and suspensions. In both tests these limiting diameters correspond to the maximum diameters at which an explosion occurred. The points corresponding to a Koenen test limiting diameter of 0.50 mm or to a MVPT limiting diameter of 25 mm are merely illustrative since they correspond to those cases in which there was no explosion with a diameter of 0.75 mm or 30 mm, respectively. A clear increasing monotonous dependence was found, and the points corresponding to suspensions, as well as those corresponding to emulsions fitted one sole curve.



**Figure 4. MVPT limiting diameter as a function of Koenen test limiting diameter for suspensions (triangles) and emulsions (circles).**

As it has been proposed, the minimum burning pressure test, as an alternative test to Koenen test and vented pipe test, the possible relations between these tests and MBP test have been also analysed.

Figures 5 and 6 show the minimum burning pressure versus the Koenen test limiting diameter and the modified vented pipe test limiting diameter, respectively.



**Figure 5. Minimum burning pressure as a function of Koenen test limiting diameter for suspensions (triangles) and emulsions (circles).**



**Figure 6. Minimum burning pressure as a function of modified vented pipe test limiting diameter for suspensions (triangles) and emulsions (circles).**

A total lack of correlation between minimum burning pressure and the two current tests can be observed. This result is not surprising, as it has already been indicated, except for the water content, the influences of all analysed factors showed different behaviours when compared the minimum burning pressure test with the Koenen test and the modified vented pipe test.

Furthermore, we must keep in mind that the Koenen test is used to determine the sensitiveness of a substance to the effect of intense heat under high confinement and the modified vented pipe test is used to assess the effect of exposure of a substance to a large external fire under confined, vented conditions. However, the minimum burning pressure test is used to determine the sensitiveness of a substance to the effect of intense localized thermal ignition under high pressure.

 Even though a thermal ignition is noticed in the three tests, Koenen test and vented pipe test deal with a thermal explosion or cook-off phenomenon, which is a consequence of a reaction runaway in a chemical system undergoing exothermic reaction. The condition involves the near simultaneous heating of an entire inventory followed by a rapid reaction.

On the other hand, minimum burning pressure test uses a localized ignition (hot spot) which can lead to a deflagration where pressures are sufficient to support combustion. In contrast to thermal explosion, deflagration involves the passage of a combustion wave through an energetic material, normally at ambient temperature in the unreached state. This means, an intense local thermal initiation can lead to a deflagration if local pressures are sufficient high to support this combustion process. Deflagration depends on pressure so a burning front will tend to accelerate unless there is a means of dissipating high pressures. Finally, if the comparatively slow sub-sonic burn can accelerate enough, a deflagration to detonation transition would take place.

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