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Screening procedures for reactive chemicals according to the UN Manual of Tests and Criteria, Appendix 6:  
a critical review

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The test methods and classification criteria contained in the United Nations Manual of Tests and Criteria or UN MTC (United Nations, 2003a), currently the 8th revised edition, have become increasingly relevant in recent years as they no longer relate only to transport classification (TDG), but also to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS). Where more and more new substances are placed on the market and thus need to be evaluated for their hazardous properties, the application of proper screening procedures and, if necessary, proper test methods has become even more important. An essential requirement is that such work is done by competent personnel and that clear procedures and criteria are available.

This paper presents an overview of the current screening procedures and criteria and identifies and addresses some common misunderstandings and misinterpretations. It also proposes a couple of possible solutions that could lead to a better use and application of these procedures. In this way, lengthy discussions between industry and authorities as well as unnecessary testing can be avoided.

* 1. Introduction

To avoid unnecessary testing and thus unnecessary costs and environmental impact, the UN MTC has long presented in its Appendix 6 a set of screening criteria that can be used to determine whether testing for e.g. explosivity, flammability, oxidizing properties or self-heating can be waived. This appendix contains a set of concise criteria. Other relevant criteria however, are more or less hidden in the text of, for example, the United Nations Recommendations on the Transport of Dangerous Goods, Model Regulations (United Nations, 2023b). It should be noted that Appendix 6 only contains screening procedures for physical-chemical hazards, not for toxicity or ecotoxicity.

Screening criteria have become increasingly important. The scope of the UN MTC has been extended from TDG to GHS and nowadays these criteria are also referred to within the frameworks of the CLP Regulation (European Union, 2023) and the Biocidal Products Directive (European Union, 2012). Moreover, the number of chemicals placed on the market and thus requiring evaluation and authorization, continues to grow. Last but not least, more and more different test institutes and authorities are involved in this process.

Over the years, experience has shown a lack of expertise among parties applying these criteria or those evaluating and approving the conclusions. There were situations where the judgment of independent experts was not trusted. This can lead (and often has led) to much debate and unnecessary testing. This is partly due to the fact that application of screening criteria cannot simply be done ‘from the book’ but requires experience, competence and sensibility. Moreover, the current wording and layout of Appendix 6 can give rise to misinterpretations.

This paper gives a brief overview of the different screening procedures and criteria and discusses a couple of situations where the screening criteria were misunderstood and/or misapplied. There were situations where authorities demanded full explosivity testing even for everyday household products. In other cases, screening criteria were very strictly applied without realizing that they do not tell the complete story. This paper also discusses the meaning of screening criteria. Do they identify when testing is required or when testing is not required? This question is answered differently and this has a significant effect on the amount of testing that is required. Finally, a potential way forward is suggested.

* 1. History

In 1984, the first edition of the ‘Recommendations on the Transport of Dangerous Goods, Tests and Criteria’, was adopted and later published. Today, this publication is simply known as the ‘Manual of Tests and Criteria’ (MTC). The reference to the Recommendations on the Transport of Dangerous Goods was dropped because this publication is now also relevant for the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Initially, the UN MTC included only a part of the test methods required for the classification of hazardous substances. Other methods were included in the Recommendations on the Transport of Dangerous Goods itself. After a major harmonization in the early 1990’s, all methods for physical-chemical hazards testing were included in the UN MTC. Around the same time, it was deemed necessary to introduce screening procedures. Such procedures would avoid unnecessary testing, reduce potential environmental impact and avoid high costs, the latter not only for the testing itself but also for expensive sample materials. The screening procedures were mainly developed by an ad-hoc group of the International Group of Experts on the Explosion Risks of Unstable Substances – IGUS (Mak et al., 2022). These screening procedures were included in the UN MTC as Appendix 6. Since their introduction, they have remained largely unchanged except for some editorial changes.

* 1. Screening procedures
     1. Purpose

This paper mainly focuses on the screening procedures included in Appendix 6 of the UN MTC. However, it should be noted that some screening criteria are included in other publications. Sometimes these are not true screening criteria but rather cut-off values for classification. In practice, these cut-off values function as screening criteria because their aim is to identify whether or not new substances or formulations have to be tested for classification. This chapter provides an overview of the relevant criteria.

Screening criteria are, of course, criteria that are used to determine whether or not a substance or mixture is a candidate for classification as dangerous good. If it meets these criteria, further testing is not required. If it does not meet these criteria, the materials needs to be tested in accordance with the appropriate test methods. Screening is always related to a specific property. If the materials does not meet the criteria for a certain property (e.g. self-heating), it will still be necessary to screen this material for other properties (e.g. flammability). Moreover, some properties may be relevant for different classification possibilities. For instance, explosivity is not only relevant for classification as an explosive substance but also for classification as an organic peroxide or a self-reactive substance.

Screening is an essential part of the evaluation of the hazard potential of new substances. This includes intermediates as well as new products and mixtures and especially products in the R&D phase. Proper application of the screening procedures can minimize the need for testing. If less testing is done, less test substance will be needed. For several reasons this is important:

* In the R&D phase usually a small amount of test substance is available. A full testing procedure may require several kilograms of material, while in the R&D phase often only grams are available.
* In the R&D phase usually only limited information regarding toxicity is available. Screening for physical-chemical hazards will reduce the potential exposure of personnel and environment to the test substance.
* Products like pharmaceuticals may be too expensive to spend large amounts for testing when in the end it may appear that the products may not be suited to be placed on the market.

It is therefore essential that proper hazard screening is carried out prior to classification testing.

It should be emphasized that screening and testing should always be carried out by competent and experienced personnel, as highlighted in the various regulations.

* + 1. UN Model Regulations

Chapter 2 of the UN Model Regulation provides an extensive overview of the criteria for the classification of potentially dangerous goods in nine classes and a couple of divisions or subclasses. For some classes and divisions, not only classification criteria are presented but also cut-off values or lower limits (thresholds) for classification. As mentioned above, these cut-off limits act as screening criteria for a specific class or division. New products that meet these criteria need not to be considered for classification in that class or division. Table 1 presents an overview of these criteria. As this paper only deals with physical-chemical hazards, transport classes 6 (toxic and infectious substances) and 7 (radioactive material) are not included in this table. Class 9 is also not included as it comprises a wide variety of substances and articles.

Table 1: Cut-off limits for classification for transport in the UN Model Regulations

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Class or division (transport) | |  | Cut-off limit or criteria |  |
| 1 | Explosives |  | None |  |
| 2 | Gases |  | Physical state |  |
| 3 | Flammable liquids |  | Physical state |  |
| 4.1 | Flammable solids |  | No cut-off limits |  |
| 4.1 | Self-reactive substances |  | Not classified as such if a substance is an explosive substance, an oxidizing substance or an organic peroxide, or if it has a heat of decomposition below 300 J/g or if it has a self-accelerating decomposition temperature (SADT) above 75 °C |  |
| 4.1 | Solid desensitized explosives |  | No criteria |  |
| 4.1 | Polymerizing substances |  | Not classified as such if a substance has a heat of decomposition below 300 J/g or if it has a self-accelerating polymerization temperature (SAPT) above 75 °C or if it meets the criteria of another class |  |
| 4.2 | Substances liable to spontaneous combustion |  | No cut-off limits |  |
| 4.3 | Substances which in contact with water emit flammable gases |  | No cut-off limits |  |
| 5.1 | Oxidizing substances |  | No cut-off limits |  |
| 5.2 | Organic peroxides |  | Only relevant for substances with the R-O-O-R’ structure, which are not classified if they contain <1.0% available oxygen from the organic peroxide and ≤1.0% hydrogen peroxide or if they contain <0.5% available oxygen from the organic peroxide and >1.0% but ≤7.0% hydrogen peroxide |  |
| 8 | Corrosive substances |  | No cut-off limits |  |

As can be seen from this table, basic cut-off limits for classification mainly apply for self-reactive substances, polymerizing substances and organic peroxides. Other substances and substances that do not meet these criteria should be tested unless they meet the formal screening criteria that are included in Appendix 6 of the UN MTC.

* + 1. UN Manual of Tests and Criteria

Appendix 6 of the UN MTC is entirely dedicated to the screening of the hazard potential of new substances prior to classification testing. The following groups of substances are identified and screening procedures are presented.

For substances which may have explosive properties, the absence of potentially explosive properties can be identified on basis of three screening criteria:

(a) if no chemical groups associated with explosive properties are present, or

(b) if the oxygen balance does not indicate the presence of explosive properties, or

(c) if the exothermic decomposition energy is below 500 J/g while the onset temperature is not above 500 °C.

Detonation testing can be waived if the exothermic decomposition energy is below 800 J/g.

The list of chemical groups that is given as examples of groups indicating explosive properties is an excerpt from one of the older editions of Bretherick’s Handbook of Reactive Chemical Hazards.

For mixtures which may be flammable liquids, a calculation procedure can be applied for determination of the flashpoint of known flammable liquids. However, as this method requires input of several parameters, it may be faster, cheaper and even more reliable to determine the flashpoint experimentally. Cost and sample amount for a flashpoint test are relatively low. This property is not further discussed in this paper.

For substances which may be self-reactive substances, the absence of potential self-reactivity can be identified on basis of three screening criteria:

(a) if no chemical groups associated with self-reactive properties are present, or

(b) if the self-accelerating decomposition temperature (SADT) is higher than 75 °C, or

(c) if the exothermic decomposition energy is below 300 J/g.

The latter two criteria are in fact the cut-off limits that are given in the classification chapter of the UN Model Regulations.

For substances which may be polymerizing substances, straightforward criteria are given that in fact reflect the typical structure of reactive monomers. This is not further discussed in this paper.

Potentially pyrophoric properties may be determined on basis of experience during production and handling, i.e. such substances will most likely already exhibit those properties during handling in the R&D phase. Potentially self-heating properties may be determined on basis of applicable screening tests, i.e. the Grewer oven test or the Gibson-Harper-Rogers test. Thus, such properties cannot be screened on a theoretical basis but the potential presence should be determined on the basis of testing. The advantage of the screening test is that it requires much less test substance than UN test N.4, which is the formal classification test (grams versus kilograms).

Substances which in contact with water may react to emit flammable gases can be screened based on the chemical structure of the substance, experience during production and handling and known information about its solubility in water.

For substances which may be oxidizing substances, testing may be waived on basis of an evaluation of the chemical structure of the substance. Only the presence of oxygen or halogen atoms is relevant.

Organic peroxides are the only group of hazardous substances that are identified primarily on the basis of their chemical structure (i.e. the R-O-O-R’ structure), rather than on basis of certain properties. Secondly, the screening procedure refers to the cut-off values that are included in the classification chapter of the UN Model Regulations. It should be noted that such substances are organic peroxides by definition because of their structure but are not necessarily classified as such. Thus, there is a difference between their chemical designation and their hazard classification.

* + 1. Guidance on the Application of the CLP Criteria

In 2009, the European Chemicals Agency (ECHA) published the first edition of its Guidance on the Application of the CLP Criteria. The aim of this document was to provide guidance for the classification and, if necessary, the testing of new substances and mixtures. The background to this publication was the complexity of the CLP Regulation itself. Under the responsibility of ECHA, the guidance was drafted by experts from research institutes, authorities and industry. The document was updated several times and a major update was published in November 2024. Part 2 of this document deals with physical hazards as represented by the seventeen hazard classes of the CLP Regulation and the GHS. For each hazard class, a paragraph ‘Screening procedures and waiving of testing’ is included. These paragraphs basically copy the information contained in Appendix 6 of the UN MTC but on several occasions they just give some additional explanation that is missing in the UN MTC. In general, the CLP Guidance gives a considerable amount of background information regarding the classification of hazardous substance that is not available in the UN Model Regulations. It seems that the UN Model Regulations implicitly assume that people dealing with classification have sufficient knowledge and expertise while the CLP Guidance observes that additional information is needed. On a number of occasions, the CLP Guidance underlines that due to the complexity of these issues, expert advice should always be sought when dealing with screening and classification.

Overall, the information on screening in the CLP Guidance is much better structured than in the UN MTC. Background information on classification is extensively present in the CLP Guidance and almost absent in the UN Model Regulations.

* 1. Observations

Since the last two decades, production and placing on the market of new chemical products has become the subject of more and stringent regulations, e.g. those dealing with REACH and with biocides. These regulations require that the hazard properties of such products be determined in accordance with accepted standards and that the results be evaluated by a competent authority (CA). Both the determination and the evaluation of such properties require a sufficiently high level of knowledge and expertise. Unfortunately, it appears that the required level is not always achieved within test institutes and authorities. Sometimes screening criteria are applied very strictly without keeping the complete picture in mind. Below are some of examples of misunderstandings and mistakes.

It oftens happens that already at the start of a screening, the wording of the criteria is misunderstood. The criteria indicate when testing is not necessary, i.e. it is worded in a negative sense. This is for instance the case for explosive properties: if no reactive groups are present, testing is not necessary. This criterion is often interpreted the other way around and in a very strict manner: if reactive groups are present, testing is mandatory. This is certainly incorrect. Presence of a reactive group does not necessarily mean that substance has potentially explosive properties. For example, an NO2 group is a reactive group and its presence may indicate explosive properties. However, a C16 molecule with one NO2 group will most certainly not have explosive properties. In one case, a CA has ignored the advice of an independent expert in this respect and insisted on fully testing such substance. Additional and avoidable costs were around EUR 12,000.--.

The same applies for the evaluation of explosive properties on the basis of the exothermic decomposition energy of a substance. If this energy is below 800 J/g, detonation testing is not necessary. A dossier was submitted to a CA, where the determination of the exothermic decomposition energy in triplicate gave results of 630, 830 and 700 J/g. Because of the second result, the CA insisted that the substance should be fully tested even though only one result was marginally higher than 800 J/g and the average was well below 800 J/g.

A formulation that contained less than 25% of a C5 aldehyde, less than 25% of an organic salt and more than 50% of water was evaluated. Despite an independent expert statement, the CA required full testing for explosive and oxidizing properties. Additional and avoidable costs were close to EUR 18,000.--.

An aqueous formulation containing less than 1% of peroxyacetic acid and less than 1% of hydrogen peroxide and no other constituents was evaluated. By definition, this formulation is not an organic peroxide and the hydrogen peroxide is much too low to cause oxidizing properties. The latter is substantiated by experience and by existing TDG and CLP classifications. Nevertheless, the CA required to determine the oxidizing properties experimentally.

Evaluation of an organic peroxide dossier led to an intensive discussion between a CA and an independent expert. The CA did not understand the difference between a formulation being an organic peroxide by definition just because of its chemical structure and the same formulation not needing to be classified as an organic peroxide because of its low active oxygen content.

The above examples and several others show that screening criteria are often misunderstood, even by so-called competent authorities. Apart from these misunderstandings, statements by independent experts are sometimes not accepted.

It must be said that problems are not always caused by a lack of knowledge. In some cases, the criteria are not properly formulated. Appendix 6 of the UN MTC states that explosive properties testing is not required if the decomposition energy is below 500 J/g. As mentioned above, this does not automatically mean that testing should always be done if the decomposition energy is above 500 J/g. Yet the same paragraph in Appendix 6 says that testing is required in the latter case. Thus, the text of Appendix 6 contradicts itself.

Also, Appendix 6 gives some examples of reactive groups. The original list contained in Bretherick’s Handbook of Reactive Chemical Hazards is much longer and includes nearly every chemical structure that has some energy within it. Both lists give the impression that molecules containing such groups are explosive anyway. This is certainly not the case and more guidance would be helpful.

* 1. Way forward

The screening procedures in Appendix 6 of the UN MTC provide useful information that can be used to avoid unnecessary testing. However, the correct application of the screening criteria is not always an easy task. It requires considerable experience and knowledge about physical-chemical hazards. It seems that within test institutes and authorities the necessary expertise is not always available. However, it is certainly possible to improve this situations and there are several options to do so.

Test institutes and authorities should realize that a physical-chemical hazards expert should not be evaluating toxicological properties and that a toxicologist should not be evaluating physical-chemical hazards as both require specific expertise. It seems that people too often judge outside their expertise.

Related to the previous observations: building up expertise requires education and training. It seems that not many opportunities in this area exist. Also, classification of chemical substances is not something that can be learned from the book. It also requires training on the job.

On the other hand, the usefulness of the existing provisions for screening can be questioned. Appendix 6 of the UN MTC is very concise and offers little guidance. Some recent amendments have not made the text more comprehensible. The CLP Guidance is a bit more elaborate and provides more information.

The United Nations could consider to provide more guidance on classification but this would require a major exercise. Perhaps the CLP Guidance could serve as global guidance for screening.

* 1. Conclusions
* Screening procedures help avoid unnecessary testing. If a substance meets the screening criteria, it does not need to be tested. If it does not meet the criteria, that does not necessarily mean that it has to be tested anyway. Further considerations could still lead to the decision not to test.
* Expert advice should always be sought and valued. The need for training should not be overlooked.
* The information contained in Appendix 6 of the UN MTC is limited and the wording is not always unambiguous.
* Either Appendix 6 should be rewritten or the CLP Guidance could get a more prominent position.

Note

This paper reflects the opinion of the authors at the time of writing and does not necessarily reflect the opinion of any institute, authority or government.

Abbreviations

CA – competent authority

CLP – Classification, Labelling and Packaging

ECHA – European Chemicals Agency

GHS – Globally Harmonized System of Classification and Labelling of Chemicals

IGUS – International Group of Experts on the Explosion Risks of Unstable Substances

MTC – Manual of Tests and Criteria

TDG – Transport of Dangerous Goods

UN – United Nations

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