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

27 November 2015

Sub-Committee of Experts on the Transport of Dangerous Goods

Forty-eighth session

Geneva, 30 November − 09 December 2015
Item 10 (e) of the provisional agenda
Issues relating to the Globally Harmonized System of Classification and Labelling of Chemicals: Corrosivity criteria

Proposal for revision of Chapter 2.8 of the Model Regulations

Transmitted by the expert from Canada

Purpose

1. Following up on the discussions of the 46th and 47th Sessions of the Sub-Committee of Experts on the Transport of Dangerous Goods, to propose changes to Chapter 2.8 of the United Nations (UN) Model Regulations to the UN Sub-Committee of Experts on the Transportation of Dangerous Goods (UNSCETDG).

Introduction

2. Previous work is found in and reference is made to documents:

   a. ST/SG/AC.10/C.3/2014/69–ST/SG/AC.10/C.4/2014/12;

   b. ST/SG/AC.10/C.3/2014/99–ST/SG/AC.10/C.4/2014/18;

   c. ST/SG/AC.10/C.3/2014/104;

   d. UN/SCETDG/46/INF.15–UN/SCEGHS/28/INF.7;

   e. UN/SCETDG/46/INF.35–UN/SCEGHS/28/INF.20;

   f. UN/SCETDG/46/INF.46–UN/SCEGHS/28/INF.21;

   g. UN/SCETDG/46/INF.60–UN/SCEGHS/28/INF.24;

   h. UN/SCETDG/46/INF.61–UN/SCEGHS/28/INF.25;

   i. UN/SCETDG/46/INF.71–UN/SCEGHS/28/INF.29;

   j. ST/SG/AC.10/C.3/2015/21–ST/SG/AC.10/C.4/2015/2;

   k. UN/SCETDG/47/INF.24; and,

   l. UN/SCETDG/47/INF.25.

3. This proposal builds on the work of the referenced proposals above and the discussions that took place at the 47th Session of the Sub-Committee of Experts on the

Transport of Dangerous Goods. It focuses on the classification and packing group assignment of corrosive materials for transport, and presents proposed text in keeping with the generally established structure and regulatory format of chapters found in the Model Regulations.

4. This proposal also removes references to additivity, as an interim measure, until the issues outlined in ST/SG/AC.10/C.3/2014/99–ST/SG/AC.10/C.4/2014/18, UN/SCETDG/46/INF.46–UN/SCEGHS/28/INF.21, and ST/SG/AC.10/C.3/2015/21–ST/SG/AC.10/C.4/2015/2 can be resolved in a transport context.

Discussion

Structure of the Proposed Text

5. In line with the comments raised previously in UN/SCETDG/46/INF.46–UN/SCEGHS/28/INF.21, this proposal adopts text that is aligned with the generally accepted format and presented as regulatory text; key definitions are presented first followed by the criteria for packing group assignment.

6. Paragraph 5 of UN/SCETDG/46/INF.71–UN/SCEGHS/28/INF.29 identifies that the use of the GHS text is "included with the aim of optimal global harmonization of criteria now and in the future. Despite the non-legislative style of the GHS text, several examples of successful implementation in jurisdictions exist."

7. While the expert from Canada recognises the intent, the Guiding Principles for the Development of the UN Model Regulations[1] state that one of the purposes of presenting the Recommendations on the Transport of Dangerous Goods in the form of a model regulation is "To 'recommend' the Recommendations on the Transport of Dangerous Goods to modal organizations, regional bodies and national governments (in particular those governments considering the development of national regulations affecting the transport of dangerous goods) in a form *[original emphasis]* that can be adopted with little or no modification directly into modal, regional or national regulations."

8. It is with this understanding that the emphasis on developing regulatory text remains the primary purpose of this proposal and work towards incorporating further criteria for the classification of corrosives in the UN Model Regulation. While principles and guidance are useful in discussing concerns relating to regulatory provisions, they do not readily form text that can be incorporated into regulation and that can be readily enforced.

Generic Concentration Limits

9. Previous proposals attempted to assign (generic) concentration limits for determining packing group of mixtures in Class 8A and Class 8 without sub-classification respectively.

10. Concentration alone is not an appropriate selection criterion for assigning packing group. Concentration is linked to pH for Brønsted-Lowry acids/bases and it can be a useful parameter to infer the corrosivity of a strong Brønsted-Lowry acid/base. Weaker Brønsted-Lowry acid/bases are governed by their dissociation into a liquid and this dissociation will vary with each weaker acid/base – generic concentration limits for determining corrosivity become problematic due to the huge variation in dissociation possible for weaker acids/bases. A concentration threshold is also inappropriate when considering corrosivity of Lewis acids/bases (an alternative acid/base definition).

[1] http://www.unece.org/fileadmin/DAM/trans/danger/publi/unrec/GuidingPrinciples/Guiding_Principles_Rev18.pdf

11. Given the huge variation in the types of potentially corrosive acids/bases and other substances that exist, determining generic concentration limits for corrosive substances becomes problematic and risks under- or over-classifying many types of corrosives that may be transported. It also does not take into account the effect of the corrosive substance's solvent and additives in solution, which may amplify or mitigate corrosivity – a generic concentration threshold may properly classify a specific corrosive substance in one solvent but not in another. For example, the presence of surfactants in solutions of certain household cleaning products has been found to affect the corrosivity of these products; when surfactants are contained in a product, some otherwise corrosive products no longer meet the corrosive criteria and would then be classified as irritants,[2] the opposite may also be true.

Acid/Alkaline Reserve

12. The consideration of acid/alkaline reserve is raised in the proposed text of most previous submissions. Canada supports the consideration of acid/alkaline reserve but would identify several issues with the text originally proposed in ST/SG/AC.10/C.3/2014/69–ST/SG/AC.10/C.4/2014/12 and the references to published papers such as *Young et al. (1988)*:[3]

a. While the references mentioned in the GHS[4] present peer-reviewed approaches to quantifying acid/alkaline reserve, they are not standardised approaches consistent with other standards referenced in the Model Regulations for use in classification. The lack of a standardised approach for determining acid/alkaline reserve presents a significant challenge in ensuring consistent, reproducible, and reliable results for classification of corrosive substances, and in the verification for enforcement of classification from a member state perspective. The lack of a formal standard for determination of acid/alkali raises issues of reproducibility and consistency of data.

b. More recent work on acid/alkaline reserve has built on the works referenced in the GHS. For example, the *Craan et al. (1997)*[5] paper has built on and furthered the body of work on acid/alkaline reserve. Of note, *Craan et al. (1997)* proposes an alternative definition for corrosives incorporating pH and acid/alkaline reserve based on thresholds and varying the acid/alkaline reserve ranges based on whether the substance is a solid or liquid. As well, it makes note of the impact additives (e.g., surfactants) can have in altering the validity of these ranges and revealed an

[2] *Craan A. J., Sanfaçon G., Walker R. H. (1997): The use of pH and acid/alkaline reserve for the classification and labelling of household cleaning products: data from a poison control center. International Journal for Consumer Safety Vol. 4, Iss. 4, 191-213.*

[3] *Acid/Alkaline reserve may be determined e.g. by the methodology detailed in Young J.R., How M.J., Walker A.P., Worth W.M.H. (1988): Classification as corrosive or irritant to skin of preparations containing acidic or alkaline substances, without testing on animals. Toxicology in Vitro 2, 19-26 and Young J.R., How M.J. (1994): Product classification as corrosive or irritant by measuring pH and acid / alkali reserve. In Alternative Methods in Toxicology vol. 10 - In Vitro Skin Toxicology: Irritation, Phototoxicity, Sensitization, eds. A.Rougier, A.M. Goldberg and H.I.Maibach, Mary Ann Liebert, Inc. 23-27.*

[4] *Ibid.*

[5] *Craan A. J., Sanfaçon G., Walker R. H. (1997): The use of pH and acid/alkaline reserve for the classification and labelling of household cleaning products: data from a poison control center. International Journal for Consumer Safety Vol. 4, Iss. 4, 191-213.*

asymmetric distribution along the pH axis of six classes of consumer products, which deviates from the proposal presented in *Young et al. (1988)*.[6]

13. Consideration of acid/alkaline reserve is maintained in the proposal below 2.8.4.2.3, however consideration should be given to the development of a standard test method that can be adopted into the Model Regulations. Canada's Department of Health has done some work towards developing such a method, Annex C contains the relevant text for discussion and future work.

Additivity and Dilution

14. The additivity approach presented in 2.8.2.3.3.2 of ST/SG/AC.10/C.3/2014/69–ST/SG/AC.10/C.4/2014/12 does not account for potential synergistic effects (as discussed in paragraph 12 above) between corrosive substances in a mixture. The additivity approach presented in the GHS assumes a simple additive relationship between components, which may not be the case; mixtures of components may result in a corrosivity that is greater than or less than the sum of the individual components. Additional investigation of these interactions needs to be conducted and quantification of interactions needs to be developed (along with guidance on impacting factors) before this approach could successfully be brought into a regulatory context. Any data or research that can be contributed to this discussion by members of the UNSCETDG or the UNSCEGHS would be welcomed for consideration.

15. The dilution approach presented in 2.8.2.3.2.2 of ST/SG/AC.10/C.3/2014/69–ST/SG/AC.10/C.4/2014/12 states that a corrosive substance diluted with another corrosive substance that has an equivalent or lower corrosivity classification would be classified as equivalent to the original corrosive substance; this does not take into account for potential additivity impacts.

16. The proposed text in the annex specifies dilution as the process of diluting a corrosive with a non-corrosive, and would need to account for the impact of additives in the diluent as discussed in paragraph 15. Dilution with another corrosive may raise additivity issues and should not be considered under dilution.

Proposal for discussion

17. In light of the above, it is proposed that Chapter 2.8 of the Model Regulations be replaced with the text in the attached Annex A to this document. The proposed section is aligned with the general format and approach utilised in the Model Regulations. It focuses on the packing group assignment of corrosive materials for transport and proposes further steps towards harmonisation with Chapter 3.2 of the GHS.

18. Annex B presents the proposal with new text underlined and deleted text crossed-out.

[6] *Young J.R., How M.J., Walker A.P., Worth W.M.H. (1988): Classification as corrosive or irritant to skin of preparations containing acidic or alkaline substances, without testing on animals.*

ANNEX A

CHAPTER 2.8

CLASS 8 – CORROSIVE SUBSTANCES

2.8.1 Definition and general provisions

2.8.1.1 *Corrosive substances* are substances which, by chemical action, will cause irreversible damage to the skin or, in the case of leakage, will materially damage, or even destroy, other goods or the means of transport.

2.8.1.2 For substances and mixtures that are corrosive to skin, hazard classification is determined using criteria in section 2.8.2, where they will be assigned to a packing group.

2.8.1.3 Substances and mixtures which do not meet the GHS criteria for Category 1 (skin corrosion) may be considered as not dangerous for transport with regards to Class 8.

2.8.1.4 Liquids, and solids which may become liquid during transport, which are judged not to be skin corrosive shall still be considered for their potential to cause corrosion to certain metal surfaces in accordance with the criteria in 2.8.2.6 (c) (ii).

2.8.2 Assignment of packing groups

2.8.2.1 Substances and mixtures of Class 8 are divided among the three packing groups in accordance with the following criteria:

(a) *Packing group I:* Very dangerous substances and mixtures;

(b) *Packing group II:* Substances and mixtures presenting medium danger;

(c) *Packing group III*: Substances and mixtures presenting minor danger.

2.8.2.2 Allocation of substances listed in the Dangerous Goods List in Chapter 3.2 to the packing groups in Class 8 has been made on the basis of experience taking into account such additional factors as inhalation risk (see 2.8.2.3) and reactivity with water (including the formation of dangerous decomposition products). New substances, including mixtures, can be assigned to packing groups on the basis of the length of time of contact necessary to produce full thickness destruction of human skin in accordance with the criteria in 2.8.2.4.

2.8.2.3 A substance or mixture meeting the criteria of Class 8 having an inhalation toxicity of dusts and mists (LC_{50}) in the range of packing group I, but toxicity through oral ingestion or dermal contact only in the range of packing group III or less, shall be allocated to Class 8 (see note under 2.6.2.2.4.1).

2.8.2.4 In assigning the packing group to a substance in accordance with 2.8.2.5, account shall be taken of human experience in instances of accidental exposure. In the absence of human experience the grouping

shall be based on data obtained from experiments in accordance with OECD Test Guideline 404[1] or 435[2]. A substance which is determined not to be corrosive in accordance with OECD Test Guideline 430[3] or 431[4] may be considered not to be corrosive to skin for the purposes of these Regulations without further testing.

2.8.2.5 Packing groups are assigned to corrosive substances in accordance with the following criteria:

(a) *Packing group I* is assigned to substances and mixtures that cause full thickness destruction of intact skin tissue within an observation period up to 60 minutes starting after the exposure time of three minutes or less;

(b) *Packing group II* is assigned to substances and mixtures that cause full thickness destruction of intact skin tissue within an observation period up to 14 days starting after the exposure time of more than three minutes but not more than 60 minutes;

(c) *Packing group III* is assigned to substances and mixtures that:

(i) cause full thickness destruction of intact skin tissue within an observation period up to 14 days starting after the exposure time of more than 60 minutes but not more than four hours; or

(ii) are judged not to cause full thickness destruction of intact skin tissue but which exhibit a corrosion rate on either steel or aluminium surfaces exceeding 6.25 mm a year at a test temperature of 55 °C when tested on both materials. For the purposes of testing steel, type S235JR+CR (1.0037 resp. St 37-2), S275J2G3+CR (1.0144 resp. St 44-3), ISO 3574 or Unified Numbering System (UNS) G10200 or a similar type or SAE 1020, and for testing aluminium, non-clad, types 7075–T6 or AZ5GU-T6 shall be used. An acceptable test is prescribed in the Manual of Tests and Criteria, Part III, Section 37.

NOTE: *Where an initial test on either steel or aluminium indicates the substance being tested is corrosive the follow up test on the other metal is not required.*

Table 2.8.2.5: Table summarizing the criteria in 2.8.2.5

Packing Group	***Exposure Time***	***Observation Period***	***Effect***
I	≤ 3 min	≤ 60 min	Full thickness destruction of intact skin
II	> 3 min ≤ 1 h	≤ 14 d	Full thickness destruction of intact skin
III	> 1 h ≤ 4 h	≤ 14 d	Full thickness destruction of intact skin
III	-	-	Corrosion rate on either steel or aluminium surfaces exceeding 6.25 mm a year at a test temperature of 55 ºC when tested on both materials

2.8.3 Hazard classification of substances corrosive to skin

[1] *OECD Guideline for the testing of chemicals No. 404 "Acute Dermal Irritation/Corrosion" 2002.*
[2] *OECD Guideline for the testing of chemicals No. 435 "In Vitro Membrane Barrier Test Method for Skin Corrosion" 2006.*
[3] *OECD Guideline for the testing of chemicals No. 430 "In Vitro Skin Corrosion: Transcutaneous Electrical Resistance Test (TER)" 2004.*
[4] *OECD Guideline for the testing of chemicals No. 431 "In Vitro Skin Corrosion: Human Skin Model Test" 2004.*

2.8.3.1 ***Classification based on standard animal test data***

2.8.3.1.1 A substance is corrosive to skin when it produces irreversible destruction of skin tissue following the application of the substance for up to 4 hours as per the criteria in 2.8.2.5.

2.8.3.2 ***Classification in a step-wise approach***

2.8.3.2.1 Existing human and animal data including information from single or repeated exposure shall be the first line of evaluation, as they give information directly relevant to effects on the skin.

2.8.3.2.2 [*In vitro* alternatives that have been validated and accepted can be used to make classification decisions. Internationally accepted validated test methods for skin corrosion include OECD Test Guidelines 430 (Transcutaneous Electrical Resistance Test (TER)), 431 (Human Skin Model Test) and 435 (Membrane Barrier Test Method).]

2.8.3.2.3 [Unless the consideration of acid/alkaline reserve suggests otherwise,] a substance with an extreme pH of ≤ 2 and ≥ 11.5 may be considered to meet the criteria for classification in Class 8, as generally such substances are expected to produce significant effects on the skin. This needs to be confirmed by other data, such as data from an appropriate validated *in vitro* test; without further testing, an automatic assignment to PG I would be made.

2.8.3.2.4 In some cases sufficient information may be available from structurally related substances to make classification decisions.

2.8.3.2.5 [This approach provides guidance on how to organize existing information on a substance and to make a weight of evidence decision about hazard assessment and hazard classification.]

2.8.4 Hazard classification of mixtures corrosive to skin

2.8.4.1 ***Classification of mixtures when data are available for the complete mixture***

2.8.4.1.1 Where sufficient data is available for classification, the mixture shall be classified using the criteria for substances in 2.8.2.5 as illustrated in Table 2.8.2.5.

2.8.4.2 ***Classification of mixtures when data are not available for the complete mixture: bridging principles***

2.8.4.2.1 Where a mixture has not been tested to determine its skin corrosion potential, but there are sufficient data on both the individual ingredients and similar tested mixtures to adequately classify the mixture, these data may be used in accordance with the following bridging principles. This ensures that the classification process uses the available data to the greatest extent possible in characterizing the hazards of the mixture.

(a) Dilution: Unless the consideration of synergistic or antagonistic effects suggests otherwise, if a tested mixture is diluted with a diluent which does not meet the criteria for Class 8 and does not affect the packing group of other ingredients, then the new diluted mixture may be assigned to the same packing group as the original tested mixture.

(b) Batching: The skin corrosion potential of a tested production batch of a mixture may be assumed to be substantially equivalent to that of another untested production batch of the same commercial product when produced by or under the control of the same

manufacturer, unless there is reason to believe there is significant variation such that the skin corrosion potential of the untested batch has changed. If the latter occurs, a new classification is necessary.

(c) Concentration of mixtures of packing group I: If a tested mixture meeting the criteria for inclusion in packing group I is concentrated, the more concentrated untested mixture may be assigned to packing group I without additional testing.

(d) Interpolation within one packing group: For three mixtures (X, Y and Z) with identical ingredients, where mixtures X and Y have been tested and are in the same skin corrosion packing group, and where untested mixture Z has the same active ingredients as mixtures X and Y but has concentrations of active ingredients intermediate to the concentrations in mixtures X and Y, then mixture Z is assumed to be in the same skin corrosion packing group as X and Y.

(e) Substantially similar mixtures: Given the following:

(i) Two mixtures: (X + Y) and (Z+Y);

(ii) The concentration of ingredient Y is the same in both mixtures;

(iii) The concentration of ingredient X in mixture (X+Y) equals the concentration of ingredient Z in mixture (Z+Y);

(iv) Data on skin corrosion for X and Z are available and substantially equivalent, i.e. they are the same skin corrosion packing group and do not affect the skin corrosion potential of Y.

If mixture (X+Y) or (Z+Y) is already classified based on test data, then the other mixture may be assigned to the same packing group.

2.8.5 Substances not accepted for transport

Chemically unstable substances of Class 8 shall not be accepted for transport unless the necessary precautions have been taken to prevent the possibility of a dangerous decomposition or polymerization under normal conditions of transport. For the precautions necessary to prevent polymerization, see special provision 386 of Chapter 3.3. To this end particular care shall be taken to ensure that receptacles and tanks do not contain any substances liable to promote these reactions.

ANNEX B

CHAPTER 2.8

CLASS 8 – CORROSIVE SUBSTANCES

2.8.1 Definition and general provisions

2.8.1.1 ~~*Class 8 substances (c* *C*~~*orrosive substances*~~*)*~~ are substances which, by chemical action, will cause irreversible ~~severe~~ damage to the skin or, in the case of leakage, will materially damage, or even destroy, other goods or the means of transport.

2.8.1.2 For substances and mixtures that are corrosive to skin, hazard classification is determined using criteria in section 2.8.2, where they will be assigned to a packing group.

2.8.1.3 Substances and mixtures which do not meet the GHS criteria for Category 1 (skin corrosion) may be considered as not dangerous for transport with regards to Class 8.

2.8.1.4 Liquids, and solids which may become liquid during transport, which are judged not to be skin corrosive shall still be considered for their potential to cause corrosion to certain metal surfaces in accordance with the criteria in 2.8.2.6 (c) (ii).

2.8.2 Assignment of packing groups

2.8.2.1 Substances and mixtures ~~preparations~~ of Class 8 are divided among the three packing groups in accordance with the following criteria:

(d) *Packing group I:* Very dangerous substances and mixtures ~~preparations~~;

(e) *Packing group II:* Substances and mixtures ~~preparations~~ presenting medium danger;

(f) *Packing group III*: Substances and mixtures ~~preparations~~ presenting minor danger.

~~2.8.2.6~~ 2.8.2.2 Allocation of substances listed in the Dangerous Goods List in Chapter 3.2 to the packing groups in Class 8 has been made on the basis of experience taking into account such additional factors as inhalation risk (see 2.8.2.3) and reactivity with water (including the formation of dangerous decomposition products). New substances, including mixtures, can be assigned to packing groups on the basis of the length of time of contact necessary to produce full thickness destruction of human skin in accordance with the criteria in 2.8.2.4. ~~Liquids and solids which may become liquid during transport, which are judged not to be skin corrosive shall still be considered for their potential to cause corrosion to certain metal surfaces in accordance with the criteria in 2.8.2.5 (c) (ii).~~

2.8.2.3 A substance or mixture ~~preparation~~ meeting the criteria of Class 8 having an inhalation toxicity of dusts and mists (LC_{50}) in the range of packing group I, but toxicity through oral ingestion or dermal contact only in the range of packing group III or less, shall be allocated to Class 8 (see note under 2.6.2.2.4.1).

2.8.2.4 In assigning the packing group to a substance in accordance with 2.8.2.6, account shall be taken of human experience in instances of accidental exposure. In the absence of human experience the grouping shall be based on data obtained from experiments in accordance with OECD Test Guideline 404[1] or 435[2]. A substance which is determined not to be corrosive in accordance with OECD Test Guideline 430[3] or 431[4] may be considered not to be corrosive to skin for the purposes of these Regulations without further testing.

2.8.2.5 Packing groups are assigned to corrosive substances in accordance with the following criteria:

(d) *Packing group I* is assigned to substances and mixtures that cause full thickness destruction of intact skin tissue within an observation period up to 60 minutes starting after the exposure time of three minutes or less;

(e) *Packing group II* is assigned to substances and mixtures that cause full thickness destruction of intact skin tissue within an observation period up to 14 days starting after the exposure time of more than three minutes but not more than 60 minutes;

(f) *Packing group III* is assigned to substances and mixtures that:

(iii) cause full thickness destruction of intact skin tissue within an observation period up to 14 days starting after the exposure time of more than 60 minutes but not more than four hours; or

(iv) are judged not to cause full thickness destruction of intact skin tissue but which exhibit a corrosion rate on either steel or aluminium surfaces exceeding 6.25 mm a year at a test temperature of 55 °C when tested on both materials. For the purposes of testing steel, type S235JR+CR (1.0037 resp. St 37-2), S275J2G3+CR (1.0144 resp. St 44-3), ISO 3574 or Unified Numbering System (UNS) G10200 or a similar type or SAE 1020, and for testing aluminium, non-clad, types 7075–T6 or AZ5GU-T6 shall be used. An acceptable test is prescribed in the Manual of Tests and Criteria, Part III, Section 37.

NOTE: *Where an initial test on either steel or aluminium indicates the substance being tested is corrosive the follow up test on the other metal is not required.*

Table 2.8.2.5: Table summarizing the criteria in 2.8.2.5

Packing Group	***Exposure Time***	***Observation Period***	***Effect***
I	≤ 3 min	≤ 60 min	Full thickness destruction of intact skin
II	> 3 min ≤ 1 h	≤ 14 d	Full thickness destruction of intact skin
III	> 1 h ≤ 4 h	≤ 14 d	Full thickness destruction of intact skin
III	-	-	Corrosion rate on either steel or aluminium surfaces exceeding 6.25 mm a year at a test temperature of 55 ºC when tested on both materials

[1] *OECD Guideline for the testing of chemicals No. 404 "Acute Dermal Irritation/Corrosion" 2002.*
[2] *OECD Guideline for the testing of chemicals No. 435 "In Vitro Membrane Barrier Test Method for Skin Corrosion" 2006.*
[3] *OECD Guideline for the testing of chemicals No. 430 "In Vitro Skin Corrosion: Transcutaneous Electrical Resistance Test (TER)" 2004.*
[4] *OECD Guideline for the testing of chemicals No. 431 "In Vitro Skin Corrosion: Human Skin Model Test" 2004.*

2.8.3 Hazard classification of substances corrosive to skin

2.8.3.1 Classification based on standard animal test data

2.8.3.1.1 A substance is corrosive to skin when it produces irreversible destruction of skin tissue following the application of the substance for up to 4 hours as per the criteria in 2.8.2.5.

2.8.3.2 Classification in a step-wise approach

2.8.3.2.1 Existing human and animal data including information from single or repeated exposure shall be the first line of evaluation, as they give information directly relevant to effects on the skin.

[2.8.3.2.2 *In vitro* alternatives that have been validated and accepted can be used to make classification decisions. Internationally accepted validated test methods for skin corrosion include OECD Test Guidelines 430 (Transcutaneous Electrical Resistance Test (TER)), 431 (Human Skin Model Test) and 435 (Membrane Barrier Test Method).]

2.8.3.2.3 [Unless the consideration of acid/alkaline reserve suggests otherwise,] a substance with an extreme pH of ≤ 2 and ≥ 11.5 may be considered to meet the criteria for classification in Class 8, as generally such substances are expected to produce significant effects on the skin. This needs to be confirmed by other data, such as data from an appropriate validated *in vitro* test; without further testing, an automatic assignment to PG I would be made.

2.8.3.2.4 In some cases sufficient information may be available from structurally related substances to make classification decisions.

[2.8.3.2.5 This approach provides guidance on how to organize existing information on a substance and to make a weight of evidence decision about hazard assessment and hazard classification.]

2.8.4 Hazard classification of mixtures corrosive to skin

2.8.4.1 Classification of mixtures when data are available for the complete mixture

2.8.4.1.1 Where sufficient data is available for classification, the mixture shall be classified using the criteria for substances in 2.8.2.5 as illustrated in Table 2.8.2.5.

2.8.4.2 Classification of mixtures when data are not available for the complete mixture: bridging principles

2.8.4.2.1 Where a mixture has not been tested to determine its skin corrosion potential, but there are sufficient data on both the individual ingredients and similar tested mixtures to adequately classify the mixture, these data may be used in accordance with the following bridging principles. This ensures that the classification process uses the available data to the greatest extent possible in characterizing the hazards of the mixture.

(f) Dilution: Unless the consideration of synergistic or antagonistic effects suggests otherwise, if a tested mixture is diluted with a diluent which does not meet the criteria for Class 8 and does not affect the packing group of other ingredients, then the new diluted mixture may be assigned to the same packing group as the original tested mixture.

(g) Batching: The skin corrosion potential of a tested production batch of a mixture may be assumed to be substantially equivalent to that of another untested production batch of the same commercial product when produced by or under the control of the same manufacturer, unless there is reason to believe there is significant variation such that the skin corrosion potential of the untested batch has changed. If the latter occurs, a new classification is necessary.

(h) Concentration of mixtures of packing group I: If a tested mixture meeting the criteria for inclusion in packing group I is concentrated, the more concentrated untested mixture may be assigned to packing group I without additional testing.

(i) Interpolation within one packing group: For three mixtures (X, Y and Z) with identical ingredients, where mixtures X and Y have been tested and are in the same skin corrosion packing group, and where untested mixture Z has the same active ingredients as mixtures X and Y but has concentrations of active ingredients intermediate to the concentrations in mixtures X and Y, then mixture Z is assumed to be in the same skin corrosion packing group as X and Y.

(j) Substantially similar mixtures: Given the following:

(v) Two mixtures: (X + Y) and (Z+Y);

(vi) The concentration of ingredient Y is the same in both mixtures;

(vii) The concentration of ingredient X in mixture (X+Y) equals the concentration of ingredient Z in mixture (Z+Y);

(viii) Data on skin corrosion for X and Z are available and substantially equivalent, i.e. they are the same skin corrosion packing group and do not affect the skin corrosion potential of Y.

If mixture (X+Y) or (Z+Y) is already classified based on test data, then the other mixture may be assigned to the same packing group.

2.8.5~~3~~ Substances not accepted for transport

Chemically unstable substances of Class 8 shall not be accepted for transport unless the necessary precautions have been taken to prevent the possibility of a dangerous decomposition or polymerization under normal conditions of transport. For the precautions necessary to prevent polymerization, see special provision 386 of Chapter 3.3. To this end particular care shall be taken to ensure that receptacles and tanks do not contain any substances liable to promote these reactions.

ANNEX C

Health Canada – Development of Method C-14.2 "Determination of Acid and Alkali Reserves in Consumer Products"

Attached document.

Health Canada Santé Canada

PROJECT REPORT

Development of Method C-14.2 “Determination of Acid and Alkali Reserves in Consumer Products”

Product Safety Laboratory
Health Protection Branch
1800 Walkley Road
Address Locator: 6402A
Ottawa, Ontario K1A 0L2

2000-08-09
Project #99-0507

ANNEX C

PROJECT REPORT

Title: Development of Method C-14.2 “Determination of Acid and Alkali Reserves in Consumer Products”

Project #: 99-0507

Date: 2000-08-09

Product Description:

Project Team: Carrie Watson

Reviewed by: Bruno Marchand

Approved by: Pierre Chantal

ANNEX C

Table of Contents

Page

ANNEX C

Development of Method C-14.2 "Determination Acid and Alkali Reserves in Consumer Products"

INTRODUCTION

The recent changes to the CCCR requires the Product Safety Laboratory to develop Method C-14.2 "Determination of Acid and Alkali Reserves in Consumer Products". A preliminary study was previously done at the Product Safety Laboratory.[1] The acquisition of the PC Titrate (model # PC-1000) instrument requires that the experimental error (precision) be determined, a S.O.P be written and control charts be prepared.

"acid reserve" means the quantity in grams of an alkali expressed as sodium hydroxide, which is required to bring 100 mL of a liquid acidic product, or 100g of an acidic product in the form of a solid, paste or gel, to a pH of 4.00±0.05

"alkali reserve" means the quantity in grams of an alkali, expressed as sodium hydroxide, that is neutralized when 100 mL of a liquid basic product, or 100 g of a basic product in the form of a solid, paste or gel, is brought to a pH of 10.00 ± 0.05

1 MATERIALS AND SOLUTIONS

1.1_ Certified buffer solutions from Fisher Scientific, SCP Science and Metrpak pHydrion Buffers. pH's of 1, 4, 7, 10 and 12.45.

1.2 Electrode: Accumet (13-620-287 SN8274018)

1.3 Samples:

Seven commercially available cleaning solutions; three for acid reserve and four for alkali reserve were chosen to give different ranges in acid and alkali reserve, respectively. These consumer products reflect typical samples tested in the laboratory. i.e solids, aerosol and liquids. The seven samples included three for the determination of acid reserve (Table 1);

- D-Scale It (UPC# 6905702800) (liquid)
- Lave-Bain et Douche (UPC# not available) (liquid)
- Stoneware & Porcelain Cleaner (UPC# 2539818671)(emulsion)

and four for the determination of alkali reserve (Table 2);

- Javex Bleach (UPC#585760) (liquid)
- Ajax (UPC#5800074821) (solid)
- Easy- Off Oven Cleaner (UPC#624042) (liquid)
- Easy-Off Oven Cleaner (UPC#624002) (aerosol)

2. ANALYTICAL INSTRUMENTATION

2.1 PC Titrate (model #PC-1000) from Man-Tech Associates Inc.

3. EXPERIMENTAL PROCEDURE

3.1 Calibration Curve

The pH meter and electrode pair assembly were standardized according to the instruments manufacturer's instruction using three reference buffer solutions that closely bracketed the anticipated pH of the test sample. The slope and intercept were recorded and determined whether they fall within acceptable limits.

3.2 A certified buffer having a pH close to that of the test sample was determined.

3.3 In the case of a liquid product, a known volume of sample was dispensed from its container (neat) and titrated with the appropriate titrant . A product in the form of a solid, paste or gel or in a form otherwise unsuitable for direct measurement, a suitable aliquot of a 10% aqueous solution was titrated with the appropriate titrant.

3.4 Titrations of each of the seven test samples were performed in replicates of 10. Fresh sample was used for each titration. Depending on the pH of the sample, either an acid reserve (Table 1) or an alkali reserve (Table 2) was performed.

3.5 The standard deviation (s.d) was determined using 10 replicates of each of the seven test samples.

3.6 Of the seven samples tested, the sample with the highest %CV (coefficient of variation) was used for the determination of the repeatability. This was calculated as follows:

95% repeatability limit = 1.960 √2 CV%.

= 2.8 x 5.75 (Ajax sample)

= 16.1%

4 CALCULATIONS

Acid or Alkali Reserve for Liquids:

$$\text{g.NaOH/100mL of sample} = \frac{\text{normality of titrant (N) x vol. of titrant (mL) x 100}}{\text{vol. of sample (mL)}} \times \frac{40\text{g}}{1000\text{mL}}$$

Acid or Alkali Reserve for Solids, Pastes or Gels:

$$\text{g.NaOH/100g of sample} = \frac{\text{normality of titrant (N) x vol. of titrant (mL) x wt. of dist. water x 100}}{\text{vol. of sample (mL) x wt. of sample (g)}} \times \frac{40\text{g}}{1000\text{mL}}$$

5 RESULTS AND DISCUSSION

5.1 The precision of Method C-14.2 " Determination of Acid and Alkali" using the PC-Titrate instrument was found to have a 16% repeatability limit at a 95% probability.

5.2 Annex-1: Update of Method C-14 "Determination of Acid and Alkali Reserve in Consumer Products"

5.3 Annex 2: SOP (PC-Titrate)

5.4 Annex 3: Control Chart (PC-Titrate Instrument)

ANNEX C

Table 1

Acid Reserve on the Three Cleaning Solutions

	D-Scale It (vol. of sample titrated 5mL)		Lave-Bain et Douche (vol. of sample titrated 1.5mL)		Stoneware & Porcelain Cleaner 10% soln. from which 10mL titrated	
Replicate #	Vol. of titrant (0.1N NaOH) (mL)	g.NaOH 100mL	Vol. of titrant (0.1N NaOH) (mL)	g.NaOH 100mL	Vol. of titrant (0.1N NaOH) (mL)	g.NaOH 100g
1	9.81	0.78	10.33	2.75	9.78	3.91
2	10.01	0.80	10.17	2.71	9.79	3.91
3	9.81	0.78	10.19	2.72	9.58	3.83
4	10.01	0.80	10.32	2.75	9.57	3.83
5	10.01	0.80	10.20	2.72	9.61	3.84
6	10.01	0.80	10.34	2.76	9.81	3.92
7	10.21	0.82	10.55	2.81	9.79	3.92
8	10.01	0.80	10.15	2.71	9.78	3.91
9	10.21	0.82	10.35	2.76	9.61	3.84
10	10.21	0.82	10.36	2.76	9.61	3.84
Mean	-	0.80	-	2.74	-	3.87
Standard Deviation	-	0.01	-	0.03	-	0.04
%CV	-	1.25	-	1.09	-	1.03

ANNEX C

Table 2

Alkali Reserve on the Four Cleaning Solutions

	Javex Bleach (vol. of sample titrated 20mL)		Ajax 10% soln. from which 10mL titrated		Easy-Off (vol. of sample titrated 0.5mL)		Easy-Off (vol. of sample titrated 0.5mL)	
Replicate	Vol. of titrant (0.1N HCl (mL)	g.NaOH / 100mL	Vol. of titrant (0.1N HCl (mL)	g.NaOH / 100g	Vol. of titrant (0.1N HCl(mL)	g.NaOH / 100mL	Vol. of titrant (0.1N HCl (mL)	g.NaOH / 100mL
1	2.16	0.043	3.21	1.28	6.95	5.56	10.21	8.17
2	2.36	0.047	3.21	1.28	6.75	5.40	10.61	8.49
3	2.16	0.043	3.51	1.40	6.54	5.23	10.25	8.20
4	2.16	0.043	3.31	1.32	6.80	5.44	10.26	8.21
5	2.01	0.040	3.51	1.40	6.56	5.25	10.26	8.21
6	2.26	0.045	3.41	1.36	6.54	5.23	10.01	8.01
7	2.11	0.042	3.61	1.44	6.45	5.16	10.01	8.01
8	2.11	0.042	3.70	1.48	6.57	5.26	10.01	8.01
9	2.21	0.044	3.71	1.48	6.46	5.12	10.07	8.06
10	2.26	0.045	3.71	1.48	6.52	5.22	10.21	8.17
Mean	-	0.043	-	1.39	-	5.29	-	8.15
Standard Deviation	-	0.002	-	0.08	-	0.14	-	0.15
%CV	-	4.65		5.75		2.65		1.84

:

ANNEX C

References

1. Lalonde, Pierre., pH and Acid/Alkali Reserve Values of Various Consumer Products, Health Canada, Product Safety Laboratory, 1995, Project No. 95-0404.

2. ASTM E 177-90a Standard Practice for Use of the Terms Precision and Bias in ASTM Test Methods

ANNEX C

Annex 1

Annex 2

Annex 3