DANGEROUS GOODS PANEL

Frankfurt, 16 to 20 September 2002

Agenda Item 2: Development of recommendations for amendments to the Technical Instructions for incorporation in the 2005/2006 edition

UN 1873 PERCHLORIC ACID

(Presented by J. Code)

1. INTRODUCTION

In Packing Instruction 502 of the 11th edition of the 'United Nations Recommendations on the Transport of Dangerous Goods, Model Regulations', inner packagings for **Perchloric Acid (UN 1873**) in combination packagings were restricted to glass. The ICAO Dangerous Goods Panel (DGP) adopted this restriction in Packing Instruction 501 of the 2001/2002 edition of the ICAO Technical Instructions.

The justification for this amendment was that Perchloric Acid, packaged in *glass/earthenware* inner packagings, requires the use of metal or rigid plastic receptacles and absorbent material. However, when it is packaged in *plastic bottles* the same requirements do not apply. It was deduced "that the apparent omission must have been due to the fact that plastic inner packagings were never intended to be authorized for Perchloric Acid as it is commonly stored only in glass receptacles due to compatibility problems with metal and plastic containers."

Such a restriction precludes the ability of industry to use 'specialized' plastic, such as Teflon, inner packagings. This ruling will affect manufacturers and distributors of Perchloric Acid in North America and Europe.

This Information Paper received by SEASTAR CHEMICALS INC.,substantiates information provided in the Working Paper.

PACKAGING DESIGN REPORT RENEWAL
UN 4G/X9.0/S/00/CAN/SCI/2-89

B3.1 INTRODUCTION

Seastar Chemicals of 10005 Macdonald Park Road, Sidney, B.C. V8L 5Y2 (mailing address: PO Box 2219) has been shipping ultrapure acids and bases by ground (CTC, US DOT), air (UN/IATA) and ocean transport (UN/IMO) since 1984. This renewal report concerns the combination package used by Seastar Chemicals that consists of a plastic bottle (IP.2) inner package contained in a metal receptacle that is then packed in an outer fiberboard box (4G). This basic design has been in use since 1984 for domestic and international (US, EUROPE, AUSTRALIA, MALAYSIA, TAIWAN) for air transport. Improvements in the details have evolved in this period. Seastar Chemicals currently ships approximately 5000 bottles per year by air transport. The products are packaged on site, at the above plant location.

INTENDED USAGE

The package described in this report is intended for renewal certification for the air transport (domestic and international) shipping of dangerous goods under UN/IATA Packing groups I, II, and III (CGSB Grade X, Y, & Z). The corrosives (Class 8) with secondary risks (where applicable) of toxic (Class 6.1); flammable liquid (Class 3) and Oxidizer (Class 5.1) with secondary risk of Class 8 are detailed below.

UN NUMBER	PROPER SHIPPING NAME	CLASS	SUB RISK	PACKING GROUP	PACKING INSTR.
UN2789	Acetic acid, glacial	8	3	II	809 / 813
UN2672	Ammonia solution	8		III	819 / 813
UN1788	Hydrobromic acid 49% or less strength	8		II	809 / 813
UN1789	Hydrochloric acid	8		II	809 / 813
UN1790	Hydrofluoric acid 60% or less strength	8	6.1	II	809 / 813
UN2031	Nitric acid other than red fuming with 70% or less but more than 20% nitric acid	8		II	813
UN1873	Perchloric acid 72% or less but more than 50% acid by weight	5.1	8	I	501
UN1830	Sulphuric acid with more than 51% acid	8		II	809 / 813

B.3.2 DESIGN

GENERAL DESCRIPTION

The combination package used by Seastar Chemicals consists of a plastic bottle (IP.2) inner packaging contained

in a metal receptacle, which is then contained in a fiberboard box (4G). The Teflon bottle version of IP.2 has a preformed, slightly rigid Teflon plug, to improve the sealing characteristics. The bottles are double bagged in polyethylene bags to preserve the ultrapure nature of the product and the package, as well as to provide secondary containment against any seepage. The bagged bottles are then wrapped in a bubble wrap and tightly sealed in a metal receptacle. A maximum of two metal receptacles can be placed in one fiberboard box outer packaging. The metal cans are cushioned within the box with a minimum of 25mm of Styrofoam peanut packaging on both the top and bottom layers (drawings on hand at Transport Canada). A maximum volume of 4L may be contained in one package. Based on current IATA regulations, a maximum of 2L of the total capacity of the package is used for the shipping of UN1873, Perchloric Acid (packing group I, Packing instruction 501).

B.3.2a: MATERIAL AND CONSTRUCTION

Inner Packaging: I) IP.2 Plastic Bottle

Three types of plastic bottles are used depending on whether an acid or base is contained. Teflon FEP or PFA bottles are used for acids, while High Density Polyethylene (HDPE) bottles are used for the ammonia solutions.

The less permeable variant of Teflon, PFA or perfluoroalkoxy, is used primarily for the shipping of hydrochloric acid. This appears to limit migration of hydrogen chloride or chlorine atoms as compared to Teflon FEP. Teflon FEP (fluorinated ethylene propylene) is mainly used for the remaining acids. Teflon PFA is occasionally used when blank levels of 10 parts per trillion are required.

Supplier: xxxxx

Bottle size	Material	Torque for Closure
250mL	Teflon PFA	38 in-lb
500mL	"	38 in-lb
1000mL	"	38 in-lb
250mL	Teflon FEP	38 in-lb
500mL	"	38 in-lb
1000mL	"	38 in-lb
2000mL	"	38 in-lb
250mL	HDPE	hand tight
500mL	HDPE	hand tight
1000mL	HDPE	hand tight

Physical Characteristics of Bottles

Bottle size	Material	Diameter	Height		Weight
			To Shoulder	Overall	
250mL	HDPE	6 cm	10 cm	13.2 cm	32 g
500mL	HDPE	7.2 cm	13.5 cm	17.2 cm	55 g
1000mL	HDPE	9 cm	16.5 cm	21.5 cm	101 g

250mL	Teflon FEP	6 cm	10.5 cm14.8 cm	66 g
500mL	Teflon FEP	7.2 cm	13.5 cm19.0 cm	106 g
1000mL	Teflon FEP	9 cm	16.5 cm21.7 cm	187 g
2000mL	Teflon FEP	2 cm	19.5 cm24.6 cm	324 g
250mL	Teflon PFA	6 cm	10.5 cm14.8 cm	68 g
500mL	Teflon PFA	7.2 cm	13.5 cm19.0 cm	109 g
1000mL	Teflon PFA	9 cm	16.5 cm21.7 cm	190 g

ii) **Neck Plug (for Teflon FEP & PFA bottles)**

For the Teflon bottles, a preformed 38mm diameter Teflon PFA neck plug is used to improve the seal between the cap and bottle opening (especially for Hydrochloric acids as previously discussed).

Supplier: xxxx

Part description: 38mm Teflon PFA neck insert #1-0400-83

iii) **Plastic Bags**

Two 2-mil polyethylene bags are used to both protect the ultrapure nature of the product, and to contain any minor seepage. Closure of the bag is with an adhesive-backed plastic tape.

Supplier: xxxx

iv) **Bubble Wrap**

1/4" or 1/2" polyethylene bubble wrap (depending of bottle size) is used to cushion the bottle in the metal receptacle.

Supplier: xxxx

v) **Metal Receptacle**

For all sizes, a 6" dia. x 10" high (15cm x 25.4cm) can is used.

Supplier: xxxx

vi) **Styrofoam Packing Peanuts**

Used to cushion the metal receptacles or the top and bottom surfaces (25mm) and adjacent walls.

Supplier: xxxx

OUTER PACKAGING

Fiberboard Box: 4G

The outer packaging is a fiberboard box. This regular slotted container consists of a double-faced corrugated wall rated with a 275 psi bursting strength. A water resistant adhesive is used on the joining seam. The closure is affected by 75mm Kraft reinforced tape. The tape overlaps the sides of the box by 75 - 100 mm.

The size of the fiberboard box is such that adequate labeling for "Cargo Aircraft Only" with 2 hazard labels (primary plus secondary) can be displayed on one face. This size allows two metal receptacles to be adequately cushioned with Styrofoam peanut packing.

Supplier: xxxx

B.3.3 QUALIFICATION TESTING

B.3.3a Tests Required

The appropriate test sections of CAN/CGSB-43.150-95 that apply to a combination packaging with an IP.2 inner package and a 4G outer package are as follows:

6.1 Chemical Compatibility
6.2 Drop Testing
6.3 Compression Resistance
6.4 Internal Pressure
6.6 Water Resistance of Fiberboard

B.3.3b Test Methods and Equipment

Equipment
Weighing: Mettler analytical balance, model PJ3000
Capacity: 3.3kg precision: 0.01g
Calibration weights used
Bathroom scale: for weights in compression test.
(Calibrated against the Mettler Balance)

Temperature: Mercury-glass lab thermometer, range -30^0 c to 100^0 (precision $+0.1^0$C)

Temperature/Relative Humidity: Springfield analog, range - 20^0 to $+50^0$ C and 10% to 100% RH, precision 1^0C, 1% RH.

Walk-In Freezer: Coldmatic Refrigeration for conditioning samples for drop test,
Range: -40^0 C to $+40^0$ C precision: 2^0 C

Pressure/Regulator: USG, 100kPa full scale, 5 kPa division, maximum pressure rating
250 kPa

TEST METHODS

6.1 Chemical Compatibility

a) Long term storage at room temperature (18 - 27^0 C). A variety of Teflon bottles containing acids have been in use continually since 1984. Until the past two years, the majority has been comprised of the Teflon FEP resin. For ammonia solutions, HDPE bottles have been in use on a continuous basis for 3-4 years. It should be noted that these bottles undergo an initial leaching in hot acids (60^0 C) for 3 weeks prior to use. Generally, the quality and "usefulness" of Teflon bottles increases with age and continued exposure or leaching by acids.

b) High temperature test: 60^0 C for 2 weeks. Bottles were triple bagged in polyethylene and placed in a hot water bath normally used for hot acid leaching of Teflon and HDPE bottles. Acid/base samples were used to evaluate leaching of trace metals in this ultrapure product. Note that outer packaging/metal receptacles were not compatible with this hot water bath.

6.2 Drop Testing

The method used herein is a combination of the normal periodic IATA testing, plus those required by US DOT (CFR 49) for exemption packaging. Here, drop tests are carried out every six months on 4 - 8 packages of each size of bottle. Packages, subjected to standard temperature and humidity, (21-23^0 C, 62-65% RH) are dropped from a height of 2.8m (Grade X, Perchloric acid has a density of 1.6g/cm^3; Grade Y, Sulphuric acid has a density of 1.8g/cm^3) onto a flat concrete floor. However, rather than one drop per package for each face plus the bottom joint corner, the testing was extended so that each package was dropped a total of 7 times - once per flat surface of the box and once on the bottom joint corner.

The procedure was repeated with 4 new packages but preconditioned at low temperatures (-20^0 C) for 24 hours. An antifreeze solution was used to prevent ice formation. A walk-in temperature controlled freezer was used for attaining this temperature. Packages were drop tested immediately after removal from the freezer. A total of eight packages were tested to cover all bottle sizes and types.

6.3 Compression Resistance (Stackability)

For the compression testing, an actual stacked load was used on four samples. The constant load mass was calculated assuming the maximum density product shipped (sulfuric, d=1.8g/cm^3) and maximum net volume per package (4L). Thus, for a package about 316mm high weighing 9.0 Kg, the required mass of the constant load is: M = 9.0 (3000-316)/316= 76.4 kg. A much higher load was applied. An actual load of 125kg/package was achieved by distributing a load of 448 kg (the composite of aliquots of water collected in two drums were summed up from the weights obtained on a calibrated bathroom scale).

The filled drums were placed on two pallets (55kg) placed back to back to distribute the pressure evenly over the four packages. The initial height of each package was recorded before and after the load was applied, and then at intervals afterwards until 24 hours was reached. After the constant load was removed, two filled packages were placed on the compressed sample and allowed to stand for 1 hour.

6.4 Internal Pressure

To validate the test packagings plastic bottles for a 100 kPa rating, a hydrostatic pressure of greater or equal to 100 kPa was applied to the sealing surface. This was performed using air pressure to force the liquid in the bottle up against the seal.

Here, a pneumatic air line was used to supply the required pressure to the inner packaging filled with water. The pressure was applied to the inverted plastic bottle via a pressure fitting in the cap. As the bottle and part of the line were completely filled with water, any errant air bubbles would accumulate at the end remote from the sealing surfaces. This internal pressure hence provided the required hydrostatic pressure on the seal.

In the case of the Teflon bottle, the test was conducted with and without the Teflon plug insert. The HDPE bottles do not appear to require plugs. Furthermore, ramping up the air pressure at 25kPa/min. was compared with an ‘immediate’ application of 100 kPa. Four samples of each bottle size/type were tested at 100 kPa for 30 minutes. A paper towel placed under the cap of the inverted bottle was used to help detect any seepage.

6.6 Water Resistance of Fiberboard

The outer fiberboard box was tested for water resistance using the Cobb test, ISO 535-1976E by the MacMillan

Bathurst laboratory. MBI produces the fiberboard used by BC Shippers Supplies in producing Seastar's boxes.

9.8 Leakage Test

While a leakage test was not specifically required in table 1, CGSB-43.150-95, for inner packaging, we have found that this is a very useful screening test in Seastar's ongoing QA/QC program (in accordance with CAN3-Z299.3,.4-85) with respect to the quality of manufacturing of the critical sealing surfaces. Traceability to the actual machine or die used to make that bottle hence allows corrective measures to be taken in the actual production of the Teflon bottles.

Four samples of each size and type of bottle were subjected to 110 kPa air pressure via a fitting in the cap. Pressurized bottles were held underwater for 30 minutes and inspected for bubbles.

Pressure Requirements for Testing

Vapour pressure data for the various acids and base were compiled from the scientific literature. Using formulae related to the vapour pressure at 50^0 C and that for 55^0 C produced comparable results. The highest value was 72 kPa for the packing group III products, 20% ammonia solution. Ironically, the packing group I product, perchloric acid, has a very low vapour pressure (less than 1 kPa at 20^0 C). Therefore, 100 kPa covered the above pressures and CGSB/IATA requirements. Samples were tested at 110 kPa for a measure of confidence and safety.

Sampling

Samples were randomly selected from the suppliers normal semi annual production run. An attempt was made to maximize the number of 'lots' sampled (as determined by mold number or machine number). These are thought to be representative of the packages produced.

Bottle Size	Type	Qty Tested	Mass as Net	Tested Gross
250 mL	Teflon FEP	4	1.2 kg	2.2 kg
500 mL	Teflon FEP	4	2.4 kg	3.4 kg
1000 mL	Teflon FEP	4	2.4 kg	3.4 kg
2000 mL	Teflon FEP	4	4.6 kg	5.6 kg
250 mL	Teflon PFA	4	1.2 kg	2.2 kg
500 mL	Teflon PFA	4	2.4 kg	3.4 kg
1000 mL	Teflon PFA	4	2.4 kg	3.4 kg
250 mL	HDPE	4	1.1 kg	2.1 kg
500 mL	HDPE	4	2.2 kg	3.2 kg
1000 mL	HDPE	4	2.2 kg	3.2 kg
Note: Water used for filling bottles for testing				

B.3.3c TEST RESULTS

6.1 Chemical Compatibility : PASS

Packages (IP.2) do not show evidence of stress cracking or crazing, oxidation, embrittlement, vapour pressure buildup, collapse of walls, seepage or other defect likely to cause or indicate premature failure. The Teflon bottles appear to have a life span of greater than 9 years under normal conditions. Teflon bottles that were in use during Seastar's inception in 1984 are still serviceable. Aesthetically, they lack the clarity of new production;

but as a result of longer leach times, still remain clean. No discolouration of the Teflon was noted in the hot leach testing. After a couple years of service, the Teflon slowly becomes milky white in colour when exposed to nitric acid; and, turns a slight greenish yellow hue (translucent) when exposed to hydrochloric acid. This discoloration is diminished, but not eliminated, by the use of the less permeable Teflon PFA. The mechanical properties of the bottle appear unaffected. The remaining acids do not impart any colouration.

The HDPE bottles containing ammonia solutions do not show any apparent changes in mechanical properties when stressed at room temperature for 1 - 2 years or at 60^0 C for two weeks. In both cases, the bottles do discolour to a pale yellow-brown, and the caps take on a yellow, translucent hue. However, embrittlement is not suggested. In nine years of experience in shipping ammonia solutions in HDPE by air or ground, Seastar has not had any complaints regarding leakage or premature failure.

6.2 Drop Test : PASS

All eight packages, each containing a different bottle size, handily pass our modified drop test for both standard temperature and for low temperatures. No leakage occurred from any of the bottles after 7 drops per package from a height of 2.8m. This corroborates previous testing (Sept. 1984 early tests were from 1.8m; 1989 on, tests were from 2.4m; 1993 2.6m; and currently 2.8m).

Damage to the package was limited to the outer fiberboard in the case of 250mL & 500ml along with minor denting of the metal receptacle in the case of 1 & 2L packages. The fiberboard box displayed its worst damage when dropped on the joint bottom corner, wherein the fiberboard was compressed slightly from its original shape. The reinforced sealing tape had some tearing in the 500ml 1 & 2L boxes, but no tear pattern was visible. In all cases, none of the internal contents escaped, even after the 7th drop.

Damage to the metal receptacle did not affect the seal on the lid. Some denting occurred on the unsupported side in proximity to the box wall or to the bottom. From photographs taken of the packaging before and after, it is apparent that the damage to the package is minimal and almost entirely confined to the outer package and metal receptacle.

6.3 Compression Resistance (stability): PASS

The four packages used in the 24 hour test showed only a minor deflection of (3mm) of the top surface from its original unloaded height (318mm) and its initial compression height (315mm). No other deformation of the packages was noted either externally or internally. Three filled boxes placed on top of the compressed version of the package did not move perceptibly after 60 min.

6.4 Internal Pressure (Hydrostatic Pressure Test): PASS

Note: Passes test at 110 kPa. Certification value 100 kPa Class X (Packing Group I) capable.

The test results for the internal pressure are presented in the following table. These include the pneumatic/hydrostatic approach (110 kPa) for HDPE bottles, Teflon FEP & PFA bottles with or without the Teflon plugs.

The rate of pressure application from 25 kPa/minute or 100 kPa/minute did not produce any difference to leakage/non leakage of these bottles. From previous testing, the quality of finish on the sealing surface appeared to be the most critical factor in leak resistance.

All of the Teflon bottles with or without plugs are leak tight in a hydrostatic sense for 110 kPa, and are likely good for a rating of 150 kPa or greater. A calibrated gauge to handle this pressure was not available at the time, and thus testing was confined to minor over ranging (+10%) of the 100 kPa gauge.

The HDPE bottles are all leak proof at 110 kPa, and appear to be capable of 150 kPa. They do not require

liners likely as a result of the softer, easier to mold polyethylene.

Hydrostatic Pressure Test for FEP/ PFA Teflon & HDPE Bottles

	BOTTLE		PNEUMATIC-HYDRAULIC 11O kPa TEST	
SIZE	**MATERIAL**	**QTY**	**WITH PLUG**	**WITHOUT PLUG**
250mL	Teflon FEP		PASS	PASS
500mL	Teflon FEP	4	PASS	PASS
1000mL	Teflon FEP	4	PASS	PASS
2000mL	Teflon FEP	4	PASS	PASS
250mL	Teflon PFA	4	PASS	PASS
500mL	Teflon PFA	4	PASS	PASS
1000mL	Teflon PFA	4	PASS	PASS
250mL	HDPE	4	PASS	PASS
500mL	HDPE	4	PASS	PASS
1000mL	HDPE	4	PASS	PASS

6.6 Water Resistance of Fibreboard : PASS

Outer fibreboard boxes of packagings were tested and certified by the manufacturer MacMillan Bathurst according to ISO STD 535-1976(E). Fibreboard absorbed less than 155 g/m^2 when exposed to water for 30 min.

B.3.4 CERTIFICATION:

We hereby certify that all of the requirements of CAN/CBSB-43.150-95 have been met. Tests were performed at Seastar Chemicals Inc., 10005 Macdonald Park Rd., by Garry Towle with supervision from Keri-Anne and Dr. Vidas Stukas plant manager, to the best of their abilities. The results are true and accurate.

Dated: December 1999

_____

V. Stukas (Ph.D.)
Plant Manager

Phone (250) 655-5880
Fax (250) 655-5888

B.3.5 MARKING

The continued marking for the Seastar Chemicals combination packaging that consists of:

1. A plastic bottle inner packaging rated for 100 kPa double wrapped in poly bags;
2. A metal receptacle with polyethylene bubble wrap for cushioning the bottle;
3. A fibreboard box outer packaging containing at maximum of 2 metal receptacles with a maximum volume of 4L of liquid (max. density of 1.8 g/cm^3). Packing groups I, II, & III are intended for air transport (domestic & international).

The continued marking would be as follows:

4G/X9.0/S/00/CAN/SCI/2-89
AIR APPROVED

This package when assembled under
Transport Canada approval no. SCI 2-89 meets the 100kPa Internal Test Pressure Requirement for air transport.

70% Perchloric Acid Compatibility
with Teflon PFA and FEP
May 2002

Prepared by V. Stukas, PhD
Chemical Specialist and Plant Manager at Seastar Chemicals Inc.

Introduction

Seastar Chemicals Inc. has been purifying, packaging and shipping 70% Perchloric Acid, UN 1783, throughout North America and Europe since 1985. In those 17 years of shipping acids in Teflon bottles (a fluoropolymer), there has never been a reported instance of leakage or breakage. With the discovery of Teflon and its incredible range of chemical resistance plus purity, Teflon bottles have become the standard for shipping ultrapure acids (examples of other ultrapure chemical distributors - Merck, Fisher, GFS, Seastar).

The chemical resistance of Teflon is outstanding. When exposed to oxidizing acids such as Perchloric, other (non-fluoropolymer) plastics tend to break down at the elevated temperatures used in UN testing requirements for chemical compatibility. Teflon, however, is unaffected.

Chemical Resistance Testing at Seastar Chemicals
The purity and chemical resistance of Teflon is at the core of Seastar's business. In particular, the resistance of the blow moldable Teflon FEP and Teflon PFA are exceptional.

Room Temperature:

We store 70% Perchloric Acid in Teflon bottles for several years at room temperature with no discernible effect. Note, Teflon bottled samples of the various batches produced are stored for a minimum of 3 years.

The Teflon bottles packaged for the UN drop tests withstand repeated drop tests of 3m without leakage or breakage (See Transport Canada reports for the renewal of 2-89 and/or 2-1035).

High Temperature:

The 70% Perchloric Acid is used at temperatures approaching the boiling point* in Teflon FEP and PFA bottles for our analytical work. The bottles and beakers are used continuously over several years on account of their purity. The only noticeable effect is cosmetic as the Teflon bottles become cloudy in appearance over a substantial storage time, however, the durability of the Teflon is never compromised.

**190^0 C, temperatures well above the 'high' temperature test point of 60^0 C*

— END —