TABLE 1

Physiological Effect	Threshold Ammonia Concentration	Equivalent Connector Tube Life
Least detectable odor	53 ppm	462 yrs.
Maximum concentration allowable for prolonged exposure	100	245
Maximum concentration allowable for short exposure (1/2 to 1 hour)	300-500	49-81
Least amount causing immediate irritation to the throat	408	60
Least amount causing immediate irritation to the eyes	698	35
Least amount causing coughing	1720	17
Dangerous for even short exposure (1/2 hour)	2500-4500	5-10
Rapidly fatal for short exposure	5000-10,000	2-1/2-5

REFERENCES

1. E. N. Pugh and J.A.S. Green, Metallurgical Transactions 2, 3129-3134 (1971).

2. E. N. Pugh and A.R.C. Westwood, Phil. Mag. 13, 167-83 (1966).

3. J. Halpern, J. Electrochem. Soc. 100, 421 (1953).

4. Y. Henderson and H. W. Haggard, "Noxious Gases", Chemical Catalog Co., New York, 1927.

APPENDIX

Relation Between Ammonia Concentration and Brass Corrosion Rate

It is assumed that an exposed metal surface is suspended in the vapor from an aqueous ammonia solution. A film of water containing ammonia will form on the metal surface. The film is assumed to be many molecular layers in thickness so that its properties approach those of the bulk liquid. Under these conditions the equilibrium concentration of the surface film will be the same as the liquid producing the vapor.

The experimental results discussed below are for a brass alloy containing 30% zinc. Initially the rate of weight loss is linearlv proportional to the amount of copper dissolved in the liquid contacting the metal.[1,2] This is due to the participation of cupric and cuprous ammonium complexes in the following series of reactions[1]:

1) $Cu(NH_3)_4^{2+} + e \rightarrow Cu(NH_3)_2^{+} + 2NH_3$

2) $Cu + 2NH_3 \rightarrow Cu(NH_3)_2^{+} + e$

3) $Zn + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} + 2e$

4) $2Cu(NH_3)_2^{+} + 1/2O_2 + H_2O + 4NH_3 \rightarrow 2\ Cu(NH_3)_4^{2+} + 2OH^-$

The overall reactions can be summarized as follows:

5) $Cu + 4NH_3 + H_2O + 1/2O_2 \rightarrow Cu(NH_3)_4(OH)_2$

6) $Zn + 4NH_3 + H_2O + 1/2O_2 \rightarrow Zn(NH_3)_4(OH)_2$

The cupric ammonium complex in reaction 1) removes electrons from the metal surface. This accelerates reaction 2), and the rate of the latter is equivalent to the rate of corrosive attack. One would also expect the rate of reaction 2) to increase with increasing ammonia concentration. Halpern[3] in fact found this to be the case. He studied the effect on the rate of both $[NH_3]$ and $[NH_4^+]$. Even if concentrated ammonia is diluted 1:100, less than 2% of the original NH_3 is present as NH_4^+. Halpern found the rate of reaction to vary proportionately with $[NH_3]$.

Thus if all other variables are held constant, the time required for an equivalent effect should vary inversely with the ammonia concentration. This relationship can be used to estimate minimum lifetimes for connector tubes under actual use conditions.

ACCREDITED STANDARDS COMMITTEE ON PERFORMANCE AND INSTALLATION OF GAS BURNING APPLIANCES AND RELATED ACCESSORIES

HOWARD I. FORMAN, Chairman - P. O. Box 66, HUNTINGDON VALLEY, PA 19006 - (215) 947-1154
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Comments Processed

May 2, 1985

TO MEMBERS OF SUBCOMMITTEE ON STANDARDS
FOR CONNECTORS FOR GAS APPLIANCES:

This is to inform the subcommittee that the Z21 Committee, at its April 11, 1985 meeting:

1. Returned to the subcommittee the Proposed Standard for Gas Connectors for Outdoor Connection of Fixed Appliances for Outdoor Installation and Manufactured (Mobile) Homes to the Gas Supply.

   The Z21 Committee considered the proposed standard in conjunction with correspondence from Mr. C. C. Lamar, Lamar Consultants, in which he objected to the standard on the basis it does not provide adequate coverage for evaluating the integrity and durability of protective coating materials on brass connectors. The Committee had also been provided with copies of a "background information and discussion of major provisions...." paper which had accompanied the proposed standard when it was distributed for review and comment. This paper and Mr. Lamar's letters of comment have been reviewed by the subcommittee. At the meeting Mr. Lamar and several Committee members stated similar concerns to that noted above.

   The Committee endorsed the sentiments expressed by Mr. Lamar, unanimously agreed to return the proposed standard to the connector subcommittee and hereby directs the subcommittee to report within 6 months the progress of the CPSC/GAMA ad hoc task group currently studying the subject of evaluative testing of protective coatings on connectors.

2. Returned to the subcommittee the subject of including in the date code markings the month as well as the year of connector manufacture.

   The Z21 Committee hereby directs the subcommittee to modify the connector standards to also include in the date code marking the month of manufacture, based on the final assembled product, for submittal to the Committee. The subcommittee's reason for not including the month, i.e., that parts of a connector are manufactured and assembled at different times, etc., was considered unacceptable. It was pointed out, for example, that the parts of a furnace are manufactured and assembled at different times but furnaces are provided with a month and year date code marking which has been useful in product traceability. This directive to the connector subcommittee was unanimously approved by the Committee.

3. Endorsed a project on regularization of common provisions in the standards.

   The Z21 water heater subcommittee, at its November 1984 meeting, and the Z21 thermostat and automatic ignition systems subcommittee, at its December 1984 meeting, questioned why provisions common among the standards are often stated somewhat differently from standard to standard. They agreed that coverage which is product independent logically should be the same in all standards. This project, as formulated at the February 12, 1985 meeting of the Z21 Chairman's Advisory Committee, anticipates Mr. O. C. (Red) Davis and Mr. Charles Visos (White-Rodgers) preparing the pertinent draft coverage with Mr. S. L. Blachman (A.G.A. Laboratories) as project coordinator.

   It is possible this regularization project could be in two stages: first, regularization of common provisions among the standards and, second, determine whether to form what were described as "generic" and "specific" product standards. A generic standard(s) would include provisions common among the standards. Specific product standards would reference the generic standards and include those provisions specific to the particular product. Also considered was the possibility of having a single combination control standard.

   The Committee agreed the subcommittees would be kept informed as the editorialization process progresses and that each subcommittee should establish small groups to monitor recommended changes.

If you have any questions or comments relative to the above actions of the Z21 Committee please feel free to contact us.

Very truly yours,

H I Forman

HOWARD I. FORMAN

cc: W. H. Johnson
R. J. Schulte
F. G. Hammaker
J. P. Langmead
Thomas Z. Cooper ✓
Ronald L. Medford

6(b) CLEARED 6-28-88
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REPORT

Meeting of
Working Group
of the
Z21 Subcommittee on Standards
for
Gas Appliance Connectors

Held at
GAMA Headquarters, Arlington, Virginia
June 20, 1985

Presiding: Marvin Leffler

ROLL CALL: Mr. Marvin Leffler called the meeting to order at 10:00 a.m. EDT. The following were in attendance:

Fred Hyman	Brass-Craft Manufacturing Company
Tom Cooper	Consumer Product Safety Commission
Sydney Greenfeld	Consumer Product Safety Commission
Andy Mayernik	Dormont Manufacturing Company
Jerome J. Segal	Dormont Manufacturing Company
Marvin Leffler	Flexible Fabricators, Inc.
James Brown	United States Brass Division of Household International
Guests	
Bob Crawford	American Gas Association Laboratories
Paul Lare	Artech Corp.
J. P. Langmead	Gas Appliance Manufacturers Association (Acting Secretary)

APPROVAL OF MINUTES: The minutes of the March 15, 1985 meeting were approved as circulated.

UPDATE ON CPSC ACTIVITIES REGARDING GAS APPLIANCE CONNECTORS: Mr. Sydney Greenfeld, U.S. Consumer Product Safety Commission, summarized the work which has already been done for CPSC by Artech Corp. Mr. Greenfeld indicated that Artech had examined 20 coated corrugated connectors, many of which had been more tightly coiled than the diameter of the mandrel used in the "Resistance to Ammonia Atmosphere" test in the Z21.24 connector standard. It was reported that 42% of the connectors demonstrated leakage following the test, some in parts that had been tightly coiled, some where the connectors had been bent around the specified mandrel and some in areas that had not been knowingly stressed. In all instances, there were failures in the coating permitting ammonia vapors access to the brass.

REPORT BY CPSC STAFF METALLURGIST ON POSSIBLE OVER-ANNEALING PROBLEMS: Mr. Paul Lare of Artech Corporation then reported on two new tasks which Artech will perform for CPSC. An outline of the scope of work to be performed in both Tasks 1 and 2 is attached (Attachment 1). The first task involves a study of corrosion of connectors under ammonia conditions that might occur in normal usage. He indicated that after examination of the current literature, Artech will characterize the brass from which the connectors were made and how it performs in uncommon exposures, evaluate the effects of some of the processing and testing variables on stress corrosion and attempt to relate performance to stress distribution, ammonia concentration and time of exposure.

In the second task, Mr. Lare indicated that Artech will develop a methodology to test the integrity of coatings after searching the literature and discussing the problems with the American Gas Association Laboratories (A.G.A.L.) and Underwriters Laboratories Inc. (UL). Mr. Lare informed the working group that in evaluating connector coating integrity, he will be assuming a 25 year connector life. Mr. Lare further indicated that it would be approximately 16 weeks from the start of Task 2 to its completion. This means that Task 2 of the Artech report for CPSC would be completed about the end of October.

This timetable led to a general discussion as to when the next Z21 Connector Subcommittee meeting should be scheduled. It was noted that the Z21 Committee, during its April 1985 meeting, had requested a response from the Connector Subcommittee to the connector coating issue by October. Following further discussion, it was unanimously

VOTED

> To recommend that GAMA request a postponement of the Z21 Connector Subcommittee meeting until at least after the next meeting of the Working Group which will be scheduled as soon as possible following the Artech Task 2 report.

During this discussion, the belief was expressed by several working group members that the Z21 Committee had inappropriately coupled the subject of coating integrity of connectors intended for outdoor use with the coating integrity question of connectors designed and intended for assistance in piping alignment in indoor locations. It was noted that coating integrity tests for these two distinctly different types of connectors could be quite different in view of differing exposure conditions.

DISCUSSION OF BACKGROUND AND POSSIBLE REVISION TO AMMONIA ATMOSPHERE TEST: Mr. Leffler discussed a set of tests proposed by his coating supplier for consideration as a method of determining coating adhesion. These tests suggested testing the coating on flat samples of the base metal rather than on the connector itself. It was agreed that the flat sample used should be brass.

Mr. Bob Crawford, American Gas Association Laboratories, then presented a suggested ammonia modified atmosphere test procedure. A copy of this proposed revision is attached (Attachment 2). Following discussion, it was agreed to defer further consideration of these proposed revisions until after the final Artech study is available.

Mr. Fred Hyman then discussed some testing which he had conducted on connectors. The connectors had been subjected to 20 bends around the mandrel specified in the Z21.24 standard and 5 torques as specified in that standard. These same connectors were then exposed to the ammonia atmosphere for a three hour period and none had demonstrated failure. This led to a general discussion on the need for data as to what concentration of ammonia connectors are exposed to and for what period of time.

DISCUSSION OF TESTS TO EVALUATE "AS RECEIVED" CONNECTORS: At the previous working group meeting, it was suggested that a test may need to be developed to simulate the condition of connectors which are tightly coiled in packaging. As another way of addressing this concern, it was reported that manufacturers have written to packagers of connectors and recommended changes in packaging to eliminate sharp bends. The response of one packager was demonstrated by a connector packaged in a manner that did, in fact, eliminate sharp bends.

DISCUSSION OF TEST TO EVALUATE CONNECTOR COATING: Consideration of this item was addressed under the item, "DISCUSSION OF BACKGROUND AND POSSIBLE REVISION TO AMMONIA ATMOSPHERE TEST," noted above. In determining what steps should be followed next, it was agreed that Mr. Hyman will write up a draft of the sequential testing he had performed so that similar tests could be conducted by others. This draft write-up will be distributed once it is received.

NEXT MEETING: Since the Artech report for CPSC is due to be completed by the end of October, it was agreed that the next meeting be scheduled to be held on November 14, 1985.

ADJOURNMENT: The meeting was adjourned at 1:30 p.m. EDT.

Respectfully submitted,

J. P. Langmead
Acting Secretary

JPL/lsg
Attachments (2)

CPSC-C-84-1130
PROPOSED TASK ORDER
ARTECH Reference P9485/J8450.09

ANALYSIS/TEST OBJECTIVE: To develop a correlation between the ANSI Z21.24 ammonia induced stress corrosion cracking (SCC) test relative to brass corrugated gas appliance connectors and normal ammonia exposures which can be expected to occur in the home from various commercial household cleaners.

SCOPE OF WORK: The following work shall be performed:

1. Conduct a literature search on SCC of brasses for the past 5 year period and review the state of the art testing for SCC of brass products.
2. Characterize the chemical composition, microstructure, and microhardness of the starting brass tubing material from which the corrugated tubing is formed.
3. Conduct ammonia resistance tests per Section 4.10 of the ANSI Z21.24 standard for base line purposes.
4. Modify standard test mandrel to include 3 proportionately larger diameters for test specimens and conduct testing of these formed connector specimens in the standard concentration of ammonia.
5. Analyze the exposure of connectors to indoor pollutants, particularly those produced by gas appliances, and their effect on ammonia reactivity with the connectors. Develop rationale for estimating and defining the range of ammonia exposure likely to be associated with connectors.

6. Modify standard test mandrel to include 3 proportionately smaller diameters for test specimens and conduct testing of these formed connector specimens in 3 levels of ammonia concentrations below the standard by control of the pH using H_2SO_4.
7. Subject immersed connector test samples to full strength and recommended diluted solutions of selected commercial ammonia containing household-cleaning solutions and vapor relative to results of #3-#6.
8. Subject samples of unannealed corrugated tubing to several different stress relief heat treatments and test their susceptibility to season cracking by the mercurous nitrate test per ASTM B154 as well as their resistance to ammonia induced SCC.
9. Repeat #8 for samples subjected to standard annealing practice.
10. Metallographically characterize #8 and #9 and compare with the original material (#2 above) before and after corrugation prior to heat treatment.
11. Analyze obtained data relative to the SCC of brass connectors and submit report correlating the ammonia resistance test of ANSI Z21.24 with the obtained data.

METHODOLOGY: ARTECH's approach to successfully completing the analysis/test objective stated above is dependent upon determining the time to initiate surface cracks on the variously stressed connector test specimens. Frequent careful microscopic examinations of the connectors' surfaces will be required to determine this threshold time on triplicate test specimens.

For test setup purposes, stress levels will be determined for the connectors carefully wrapped around the variously sized mandrels through the use of strain gages attached to the corrugations at critical locations. A three dimensional plot might then be possible, knowing the ammonia concentration, connector stress level, and threshold time to surface cracking, for interpolation of intermediate conditions. A duplicate set of stressed connector test specimens will be required to test the threshold time required for surface cracks to form using commercial household cleaners, since these may contain agents that change the reactivity of the ammonia. With this information established it may then be possible to test the predictability of SCC in connectors having different states of heat treatment.

The data produced is presently considered necessary prior to any design and testing of new connector test specimens that are based on a flat coil (pancake) and on a tapered coil profile of increasing diameter and therefore decreasing stress. These can be subjected to three different ammonia concentrations, for liquid and vapor states, considered likely for connector exposure in the home. Alternately flowing heated air and cooled air through the test specimen configurations to accelerate attack by heating and accelerated condensation of vapors by cooling (summertime condition) might simulate environmental conditions over a 25 year projected lifetime of the connectors. Periodic axial displacement of the coils can be incorporated into the test to simulate annual or semiannual movement of the connector.

PERIOD OF PERFORMANCE

After receiving the collected connector samples, a period of eight (8) weeks will be required to complete the laboratory work and analysis of the generated data. The additional one (1) week period will be needed to complete the draft of the final report. The final report can be delivered one (1) week after receiving approval of the draft report.

CPSC-C-84-1130
PROPOSED TASK ORDER
ARTECH Reference P10085/J8450.1Ø

ANALYSIS/TEST OBJECTIVE: To develop and demonstrate an improved methodology for evaluating organic, protective coatings for flexible gas connectors with an expected life of twenty-five years.

SCOPE OF WORK: The following work shall be performed:

1. Conduct a literature search, including phone consultations with ASTM and UL, for recent developments of the previous five (5) years in testing and evaluating life expectancy of organic coatings applied to brass. Review resulting information with CPSC staff for impact on Test Objective and Scope Of Work.

2. Obtain samples of connectors from CPSC that have little or no residual stresses and perform exploratory testing of several coated connector samples, based on the results of #1, to evaluate and demonstrate an acceptable test method, such as a conductivity change, that might be employed to monitor a change in coating protection as a function of mechanical stressing and/or chemical deterioration.

3. For base-line purposes characterize the state of coating perfection for each sample through measurement of the connector's conductivity when the coated portion is immersed in a suitable, chemically non-reacting electrolyte.

4. Form "U" shaped bends around the variously sized mandrels used in Task 09 and repeat the conductivity test to detect loss of coating integrity.

5. Axially stretch a ten-inch length near the center of the connector for several increments (one increment per connector) and remeasure conductivity.

6. Axially compress a ten-inch length near the center of the connector for several decrements (one decrement per connector) and remeasure conductivity.

7. Conduct torsion tests as contained in the ANSI Z21.24 standard and remeasure conductivity after each 90° twist and return cycle.

8. Conduct three levels of impact tests on connector samples using metallic shapes of known mass free falling from known heights and remeasure conductivity.

9. Conduct appropriate abrasion tests for several time intervals and remeasure conductivity.

10. Thermal cycle connector samples from -40°F to 300°F (maximum temperature, ANSI Z21.24) at several time intervals and remeasure conductivity.

11. Subject connector samples to concentrated and diluted household cleaners and remeasure conductivity.

12. Estimate the cyclic stresses occurring over a twenty-five (25) year period and subject connector samples to superimposed stresses that simulate yearly mechanical movement, based on results of #4 through #10 above and measure conductivity as a function of time.

13. Repeat the above incorporating the effect of household cleaning agents and/or indoor pollutants, if found detrimental in #11 above.

METHODOLOGY: ARTECH's approach to successfully accomplishing the TEST OBJECTIVE relies on a simple conductivity test to determine the existence of pores or breaks in the electrically non-conductive, organic protective coating as it exists on unstressed connectors. By intelligent selection of electrolyte concentration, electrode size, applied voltage, and instrument sensitivity, a good estimation of exposed area may be possible. Some degree of electrode polarization and other perturbations are anticipated, but electrolyte immersion is presently thought to be a means of monitoring change in the continuity of the protective coating due to imperfections (such as thin areas, bubbles, poor adhesion) that open when the connector is mechanically stressed.

Using the conductivity as a reference, determined in a suitable electrolyte, the mechanical properties of the coating can be evaluated by controlled application of forces that can be experienced by the connector during packaging, unpackaging, installation, and use over a projected twenty (25) year life. The application of these forces is expected to cause an increase in the conductivity due to mechanical breakage of the coating at a critical stress level. This methodology provides a means of determining a loss in the protection of the coating that is independent of the composition of the coating whether the loss is due to chemical or mechanical failure.

It should be noted that the forming of the "U" bend specimen for the ammonia resistance test does not address the various diameters of flexible connectors that are available. While the annealed brass is capable of deforming without failing, the stress levels incurred in the coating should be substantially different when comparing the largest diameter to the smallest diameter. Data generated during this investigation and on Task 09 should clarify this size dependency omission of the standard.

PERIOD OF PERFORMANCE

After receiving the collected connector samples, a period of twelve (12) weeks will be required to complete the laboratory work and analysis of the generated data. An additional two (2) week period will be needed to complete the draft of the final report. The final report can be delivered two (2) weeks after receiving approval of the draft report.

Proposed Revisions To Ammonia Atmosphere Test (ANSI Z21.24)

4.10 RESISTANCE TO AMMONIA ATMOSPHERE

Corrugated copper alloy metal connectors and fittings shall not develop faults which would result in gas leakage under the following Method of Test.

Method of Test

The test specified below shall be applied to each nominal diameter, type and material of connector submitted.

On connectors employing a protective coating, this test shall be conducted with the coating in place.

Four sample connectors, each 2 feet long, shall be subjected to the following conditions prior to placing in the ammonia atmosphere:

Sample No. 1 shall be subjected to a pull force of ___ pounds per inch of nominal inside diameter, using the procedure specified in 4.2.2.

Sample No. 2 shall be subjected to ___ 180° bends, using the procedure specified in 4.3.

Sample No. 3 shall be subjected to ___ 90° twists, using the procedure specified in 4.4.

Sample No. 4 shall be subjected to impacts by holding the connector horizontally and dropping from a height of ___ feet to a smooth concrete surface. This shall be repeated ___ times.

Each

~~A~~ connector shall be bent around a 2¼ inch (57.2 mm) diameter mandrel to form a "U" shape. The ends shall be secured with a nonmetallic material to hold the connector in this shape. One end of the connector shall be attached to an air supply system equipped with a manometer downstream from a shutoff valve and the other end sealed gastight. Air shall then be admitted to the connector until a pressure equivalent to 6 inches mercury column (20.3 kPa) is obtained and the shutoff valve closed.

Each

~~The~~ connector, from the back of one connector nut to the back of the opposite connector nut, shall be suspended in a sealed plastic container to which 500 milliliters of ammonia solution containing ~~250~~ milliliters of full strength ammonia (28 percent) and ~~250~~ milliliters of water have been added. (More than one connector may be placed in the container at one time.)

Note: The connector(s) must not come in contact with the ammonia solution at any time. See Figure 5.

If a sudden drop in pressure occurs, the test shall be discontinued. Otherwise, the connector shall be removed s
from the container after 18 hours and examined for leakage under not more than a 2-inch (50.8 mm) depth of water with an internal air pressure of 6 inches mercury column (20.3 kPa).

Rationale : In practice, appliance connectors and their coatings are subjected to some degree of stressing, impact and abrasion during shipping, vendor packaging and installation. The ammonia atmosphere test, which is intended to assure integrity of protective coatings, has been revised to take into account the anticipated handling of a connector prior to and during installation. The test solution concentration has been reduced ---------
(remainder of wording to be developed).

1901 North Moore Street · P.O. Box 9245 · Arlington, Virginia 22209 703/525-9565

gama

50th Anniversary

July 23, 1985

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Mr. Richard Deringer
Chairman, Z21 Connector Subcommittee
c/o Columbia Gas Distribution Companies
P.O. Box 117
Columbus, Ohio 43216-0117

Dear Dick:

On behalf of the working group established by the Z21 connector subcommittee to study connector coatings, I am requesting a postponement of the next Z21 connector subcommittee meeting presently scheduled for October 29-30, 1985.

As you know, this working group consists of the Technical Committee of the Gas Appliance Connector Group of the GAMA General Products Division and several staff members of the U.S. Consumer Product Safety Commission (CPSC). This working group has met twice already and is diligently working on the task assigned to it.

CPSC is having studies performed to examine existing connector designs in relation to variations of the ammonia atmosphere test and the continuity of the coating. The work contracted out by CPSC is scheduled to be completed at the end of September. Subsequently, the report of this project will be available 2 or 3 weeks after that.

Individual connector manufacturers also are conducting studies on connector coatings including methods of checking coating continuity and a more realistic ammonia atmosphere test. Several months are needed for manufacturers to complete this work.

On its present schedule, the working group will not have additional information to consider until the end of October. In fact, its next meeting is tentatively scheduled for November 14. Consequently, the working group will not be able to have recommendations prepared in time for consideration at the subcommittee meeting planned for October 29-30. Therefore, we

/Continued . . .

GAS APPLIANCE MANUFACTURERS ASSOCIATION, INC.