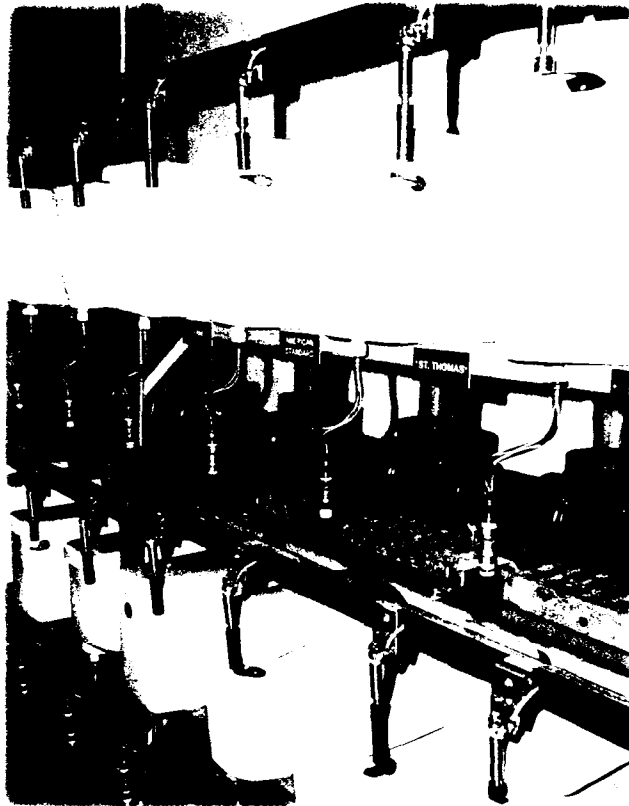


TOILET FLAPPER MATERIALS INTEGRITY TESTS



By



The Metropolitan Water District
of Southern California

May 1998

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Preface

Special appreciation and thanks for his efforts and contributions to this study go to Mr. Ron Brown, MWD Communications Division, who initiated, directed, and diligently pursued these investigations with the goal of improving the quality of the product in order to assure the durability of the water savings.

In addition, thanks to Mr. Leonard Grasha, Manager of the Corrosion Engineering Branch of the MWD Engineering Division, for making their comprehensive laboratory facilities available for this study for an extended period of time.

The ongoing expertise, advice, and work of Mr. Bill Sleeper and Mr. Harvey Webster of the MWD Corrosion Engineering Branch is also very much appreciated. These two individuals were responsible for carrying out the laboratory work in accordance with the test protocol and did so in a very professional and thorough manner.

Finally, we thank the following organizations and individuals for their contributions of products, materials, and advice for these tests:

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INTRODUCTION

Metropolitan Water District of Southern California

The Metropolitan Water District of Southern California (Metropolitan) is a California public agency. Metropolitan supplies water to 27 member agencies, which serve approximately 16 million people living within its 5,200 square-mile service area. Existing Metropolitan facilities include the 242-mile-long Colorado River Aqueduct with five pumping plants, a distribution system having seven functional reservoirs, five water filtration plants, 43 pressure control structures, 15 power plants, and approximately 775 miles of large diameter pipelines.

Metropolitan's Toilet Replacement Programs

In the early 1990s, the longest drought in California history (7 years) caused Metropolitan's allocated water supplies to be greatly limited. As a result, Metropolitan implemented a number of water conservation programs oriented to residential consumers, the most significant of which were the regional toilet retrofit programs. In these programs, customers were encouraged to replace their high volume, water-wasting toilets (with flush volumes of 3.5 gallons, 5 gallons, and higher) with new ultra-low-flush (ULF) toilets (1.6 gallons or less). Metropolitan and its participating member agencies used rebates, other toilet subsidies, and state and national legislation as the principal means of encouraging customers to retrofit their water-wasting toilets.

Toilet retrofit programs began with the onset of the drought and accelerated significantly in 1993, reaching their peak retrofit levels in 1995 (over 20,000 toilets per month). By 1997, over one million old toilets in Metropolitan's service had been replaced with new ULF toilets through water agency programs. In addition, the State of California mandated that, as of January 1, 1992, toilets installed in all new residential construction must be ULF toilets. As a further step, some communities also mandated that existing residences be retrofitted with ULF toilets upon their sale (known as "retrofit on resale" ordinances).

During this same period and in growing recognition of the urgent need to conserve the state's water supplies, the California Urban Water Conservation Council (CUWCC) defined and developed a series of water conservation measures defined as Best Management Practices (BMPs). Member water agencies throughout California (including Metropolitan) then agreed through a joint memorandum-of-understanding to pursue the implementation of those BMPs. BMP No. 14, covering residential ULF toilets, calls for aggressive replacement programs in the urban areas and provides a yardstick against which these programs are measured.

Significant water savings were being achieved as a consequence of these various actions. At the same time as retrofits were occurring, however, manufacturers and Metropolitan were receiving reports of complaints and problems with some ULF toilets in certain locales and under certain conditions. For example, toilets were leaking after being in use for only a few months, residents were required to occasionally flush their toilet more than once, and clogging was reported. (Note: Statistical data was never gathered, however, that would indicate 1.6 gallon toilets

clogged any more frequently than the 3.5 and 5.0 gallon toilets they replaced.) To overcome these problems, significant functional improvements to the toilets were being made on an ongoing basis by the manufacturers. These ongoing series of incremental improvements led to an evolution of the 1.6 gallon toilet to where the performance of the 1998 product is significantly better than that manufactured in the 1992-1995 period.

STUDY BACKGROUND

Flapper Degradation

In October 1993, Metropolitan staff met individually with five plumbing manufacturers to discuss the supply of ULF toilets to Metropolitan's distribution program. At that time, those manufacturers were experiencing severe problems with the degradation of original-equipment flush valve flappers installed in their new product. Anecdotal information was presented by the manufacturers indicating that new toilets were sometimes leaking within months of installation. In some cases, warranty demands were being made upon the manufacturers by the residential customers for repairs and/or replacements of the new ULF toilet or its internal trim. Although many of these problems surfaced in Florida and Texas at that time, they were not exclusive to that region of the country. The toilet manufacturers attributed the leaks to flappers that had rapidly degraded due to the use of certain chemically-based in-tank bowl cleaners by the residential customer¹. Nearly all of the manufacturers were already undertaking laboratory tests in their own facilities to determine the severity of and possible solutions to this problem.

To date, the retrofit of toilets in Metropolitan's service area has been the key strategy for achieving regional water conservation goals. The economics of the retrofit programs undertaken by Metropolitan were based upon a 20-year (or more) functional life of a ULF toilet. Therefore, for the projected water savings to be achieved, the ULF toilets must maintain their initial performance for that period. This, in turn, demands that flush valve flappers be comprised of materials that do not degrade and leak as a result of water conditions.

Metropolitan's Flapper Testing Program

Because of the importance of the flush valve flapper to the continuing performance of a toilet, Metropolitan undertook its own materials testing program (Program) to (1) better understand seal failure mechanisms that lead to leakage, (2) identify durable materials that could be used to withstand the chemical attacks, and (3) provide a basis for better communication with flapper and toilet bowl cleaner manufacturers. The overall purpose of the testing Program was to aid in maximizing the leak-free life of the flapper and related seals.

Initial efforts to develop the Program included an invitation to representatives of the American Society of Mechanical Engineers (ASME), American Water Works Association (AWWA), and interested water utilities to visit Metropolitan's Weymouth Treatment Plant for a general discussion of the objectives of and approach to the testing Program. Representatives of those organizations visited Metropolitan's state-of-the-art Water Quality Laboratory and Corrosion Laboratory, the latter being the site intended for establishing the Program's test facility. At that time (March 31, 1994), an official ASME/ANSI² meeting was held to discuss the Program

¹ Prior to this time, bowl cleaners were predominantly of the in-bowl type or did not contain halogenating bowl cleaners. Therefore, there was little, if any, physical effect upon the trim within the tank with the use of these cleaners..

² The ASME is the author of plumbing standards published by the American National Standards Institute (ANSI); those ASME/ANSI standards were adopted by reference and are cited in the Energy Policy Act of 1993, the law which, among other things, codified into Federal law a set of national standards for toilets' maximum water use.

and appoint a sub-committee charged with assisting in the review of a test protocol and minimum performance standards for flappers and related seals.

Corrosion Laboratory

Metropolitan's Corrosion Laboratory performs ongoing tests of the materials used in various phases of water treatment and distribution. It is one of the few laboratories dedicated to long-term testing, and results from these tests are widely distributed and valued by the water utility industry. The Laboratory has the ability to introduce various water quality levels and types of treated water to this Program not normally available to the manufacturing industry. For this reason, in addition to common goals, it has been possible to enlist the cooperation of the many groups that contributed to the Program.

Test Protocol

While there can be many causes for flush valve flapper leakage, chemical attack has been most frequently associated with flapper failure. Some in-tank bowl cleaners that contain halogenating agents can have a pronounced deteriorating effect on flappers. Those cleaners are generally one of the following two types: (a) those that use mixed halogenated methyl hydantoins and (b) those that use calcium hypochlorite. A third cleaner is a detergent-type and is not known to cause flapper deterioration (it may, in fact, promote a better valve seal in some cases). Such cleaners are widely accepted by the consumer as a means of cleaning the toilet bowl with a minimum of direct physical contact. In addition, purification chemicals for water systems, although used in much lower concentrations, can also attack flappers and elastomeric seals.

Based upon the above understanding of flapper failure, Metropolitan sought advice on test protocol development from such organizations as AWWA, ASME/ANSI, University of Akron Polymer Science Department, flapper materials manufacturers, the Clorox Corporation and numerous water utilities. A protocol was developed for the Program; it was meant to be a living document, changing as more information became available. Consequently, it was revised periodically during the course of testing; the final version of the protocol is included here as Appendix A.

Test Facility

Metropolitan also completed the equipping of a test facility within its Corrosion Laboratory that was designed specifically for accelerated and long-term durability testing on this Program. The facility included two identical test banks of nine ULF toilet tanks each, for a total of 18 tanks. (Two identical banks were installed in order to (1) duplicate failures under similar operating conditions, and (2) ensure that isolated failures in one bank would be considered unique, e.g. a manufacturing defect in the product, etc.) The 18 tanks were plumbed and equipped with a computer-controlled automatic flushing device that can be regulated to any desired flush cycle. Each bank of nine toilets contained one each of nine brands of ULF toilets typical of the Southern California marketplace and of those purchased with Metropolitan funding in 1995 for the ULF toilet distribution program. The ULF toilets tested in this Program were models

manufactured by Mansfield Plumbing Products Inc., Eljer Industries, WC, American Standard Inc., Toto Kiki USA, Inc., Crane Plumbing, Briggs Industries, Inc., St. Thomas Creations, and Kohler Company.

After equipping the test facility and prior to commencing the test protocol, industry representatives were invited to inspect the facility to ensure that each ULF toilet was properly installed and adjusted. Among those who inspected the facility were: Mr. Pat Higgins, chair of the ASME/ANSI Panel 19 - Plumbing Fixtures; Mr. Bruce Antunez, chair of the flapper subcommittee to Panel 19 and principal of Coast Foundry and Manufacturing Company; and representatives of Clorox, Lavelle Industries, Inc., Fluidmaster, Inc., Exxon Chemical Company, and Advanced Elastomer Systems.

Outside Professional Services

Further, Dr. Edward N. Kresge, a noted polymer scientist, was retained by Metropolitan to provide professional review of Program design and methodology, as well as an in-depth analysis of the various sample test materials and production flappers provided for the Program. Dr. Kresge's Curriculum Vitae are included as Appendix D.

APPROACH

The protocol calls for testing the physical properties of sheet stock material, as well as the practical properties of formed flapper configurations in a long-term “natural environment.” Thus, tests were developed for elastomer specimens under accelerated conditions and, in addition, the test facility described earlier was used for long-term durability testing of production flush valve flappers in ULF toilets.

The tests described in the protocol fall into two groups:

Accelerated Sheet Stock Test

The purpose of the accelerated testing protocol was to increase the severity of the chemical and physical environment to speed up chemical reactions that could cause flapper failure. Accelerated testing was focused on thermoset rubber and thermoplastic elastomer compounds cut from flat sheet stock or molded to American Society for Testing and Materials (ASTM) D412 Standard Dumbbell Die C specifications (see Figures 1 and 2).

Eighteen types of sheet stock compounds (or molded dumbbells) representing six different classes of elastomers were obtained from seven suppliers. Refer to Appendix E for a listing of those manufacturers and the products they submitted. The sheet stock compounds are typical of elastomers that were used in flush valve flappers in 1994 or would be a potential candidate for that application at that time.

This test called for immersing the sample dumbbells, five identical dumbbells (of the same material) per container, in a heated halogenating solution for thirty days maintained at 40° C (104° F) for the duration of the test. The solution in the containers was changed daily, from a stock supply, in order to ensure a constant concentration of halogenating solution (300 parts-per-million [ppm] in the chlorine tests). In the accelerated testing, the concentration of chlorine was considerably higher than the residual levels commonly maintained in water distribution systems (2 ppm for chloramine and 0.5 ppm for chlorine). However, it was also considerably less than the ultimate concentration of chlorine that was reached in a separate test when a tablet of Clorox Automatic® (drop-in) toilet bowl cleaner was placed in 1.6 gallons of water for an extended period of time. In this instance, after 3-1/2 months, the tablet dissolved and the chlorine concentration reached saturation at 2,312 ppm. (Note: This means that the consumer/homeowner is inadvertently causing very accelerated conditions if, before an very extended absence from the home, a tablet of toilet bowl cleaner is placed in the tank of a ULF toilet and the toilet is not flushed. Although rare, conditions approximating this scenario occur in areas, such as Florida, where “snow-birds” from the North leave their winter dwellings unused for long periods.)

The halogenating solutions were prepared from chloramine (used for disinfection in some water supplies) and two bowl cleaners: Clorox Automatic® (uses halogenated methyl hydantoins) and 2000 Flushes-Bleach® (uses calcium hypochlorite).

The samples were analyzed after exposure for weight percent swell, warping, conditions of the surfaces and cross-sections, and changes in physical properties. Swelling and warping, which usually cause a change in the valve dimensions, would be expected to alter the sealing behavior of a flapper valve. Surface roughness, blisters, cracks, etc. as revealed by microscopic examination, would also cause leaks. Changes in physical properties could lead to leaks by virtue of the material getting too hard or too soft or by complete valve failure.

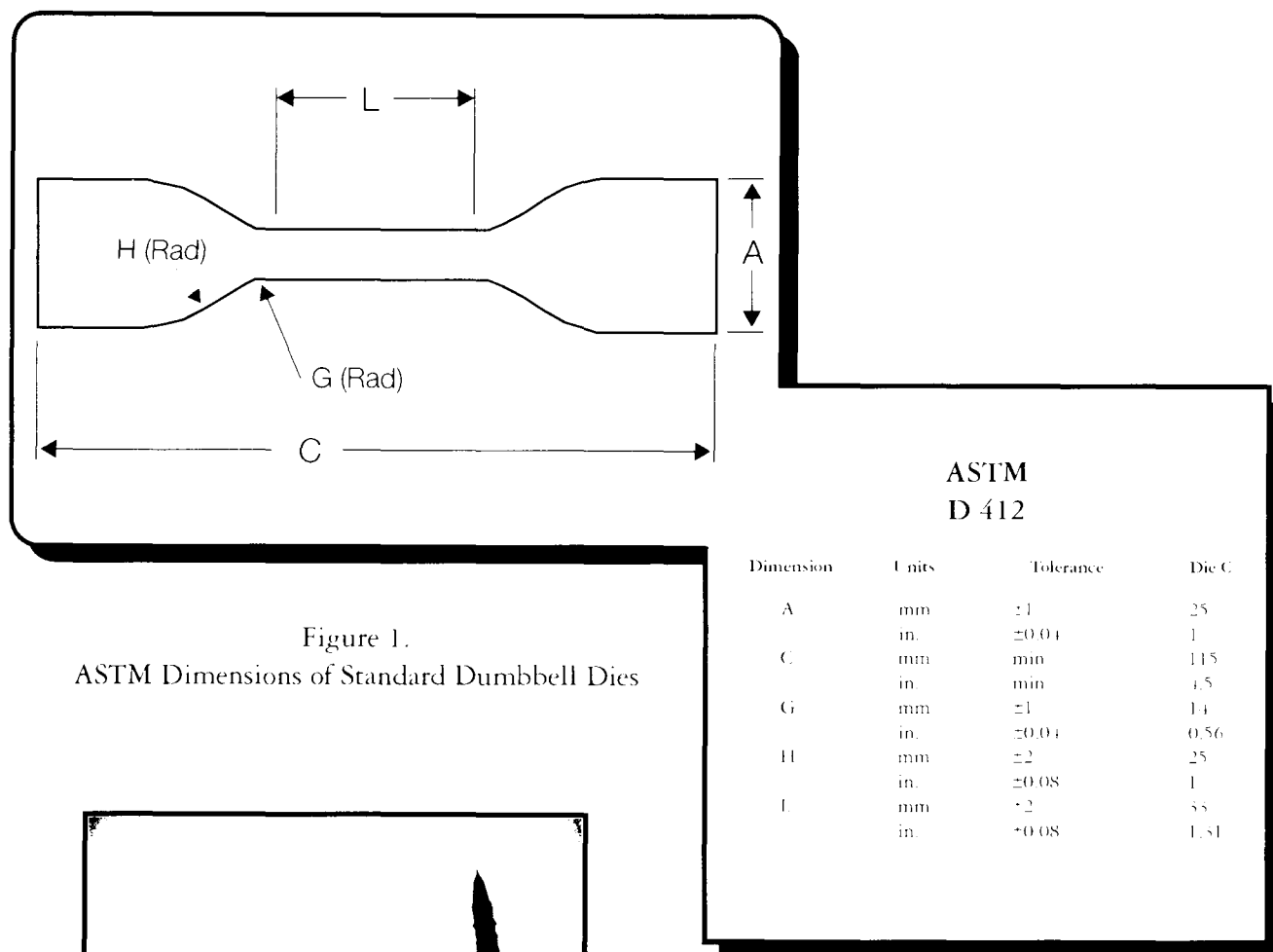


Figure 1.
ASTM Dimensions of Standard Dumbbell Dies

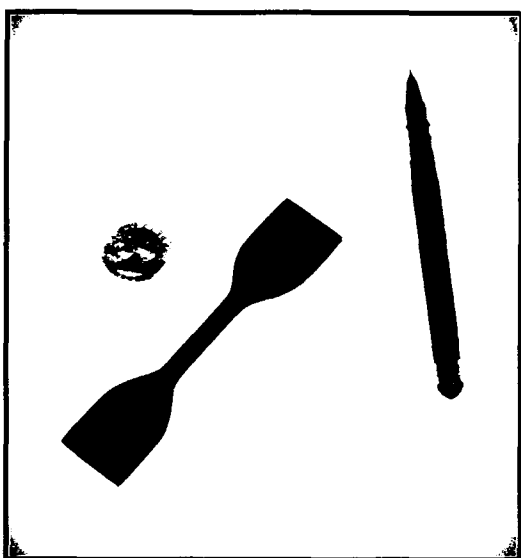


Figure 2.
Typical Dumbbell Die
Used in Accelerated Sheet Stock Test

Simulated Long-Term Aging Test

The long-term aging (durability) tests performed with the special test facility were designed to simulate 10 years of flapper performance in approximately 24 weeks. This accelerated test was run both with and without toilet bowl cleaners in the tanks.

The long-term durability test requires simulating actual household conditions as closely as possible. For this test it was assumed that the average household population in Metropolitan's service area is 2.8 people. Each of these people is estimated to flush the household toilet four times per day, creating a daily cycle of 11.2 flushes per day per household (2.8 people/household x 4 flushes/day = 11.2) .

Durability testing in tap water was conducted to (1) assess the mechanical effectiveness of existing flappers, (2) disclose any installation or start-up challenges for each of the 18 test tanks, and (3) establish a performance baseline. In this test, each ULF toilet was flushed immediately after filling for 25,000 cycles (approximately equivalent to five years of use). Refer to Appendix A for a complete description of the test protocol employed.

In the case of testing with bowl cleaners, the test was programmed to simulate a vacation or guest bathroom situation, wherein a toilet remains idle for a significant period of time, thereby allowing the chemical concentration in the tank to build up to exceptionally high levels. As noted earlier in a separate test, without periodic flushing, the tablet fully dissolves and the solution in the tank reaches saturation, resulting in a chemical concentration exceeding 2,300 ppm.

Three different bowl cleaners were tested:

- (1) Clorox Automatic® (uses halogenated methyl hydantoins)
- (2) 2000 Flushes-Bleach® (uses calcium hypochlorite)
- (3) 2000 Flushes-Blue® (detergent-based)

Appendix B contains the Material Safety Data Sheets (MSDS) for each of these products.

Leakage rates were determined at regular intervals during the test. Flappers were also analyzed after the test to assess the distortion in shape, if any, caused by swelling and a microscopic examination of the surfaces was performed. Refer to Section IV.D of Appendix A for a description of the test protocol.

SUMMARY OF TEST RESULTS

Accelerated Sheet Stock Test

All of the sheet stock compounds were attacked by the halogenating agents to some extent. This attack leads to swelling, distortion in shape, loss in physical properties, blistering, cracking, and surface tackiness, roughness, and erosion in various degrees. (See Figure 3 for an indication of the effect of long-term exposure to a bowl cleaner dropped into a 1.6 gallon tank without flushing the toilet.) These changes would be reasonably expected to lead to seal failure or leakage, the extent of which would depend upon the concentration of the halogenating agent, the exposure time, and the material's ability to withstand chemical attack.

While all of the compounds were affected by the halogenating agents to some extent, a range in performance was observed. Swelling, for example, ranged from 9.2 to 61 percent. Similarly, microscopic examination of the sheet stock revealed some samples had retained a smooth surface while others were very rough and blistered. There was a correlation of the degree of swelling and the extent of physical property retention with the results of the microscopic examination.

Of the elastomer classes tested, no single type of elastomer backbone stood out for superior performance. This indicates that performance depends on more than just the elastomer backbone type, but on other key ingredients as well, such as, curatives, plasticizers, and fillers. To establish which elastomer compounds would perform best in accelerated testing, a full compounding study would need to be carried out. To be meaningful, such a study would necessarily be a major undertaking because of the high number of variables involved.

See Appendix C for a complete report on the results of tests performed.

Simulated Long-Term Aging (Durability) Test

The results of the long-term durability test on flappers represented nine different manufacturers and two classes of elastomers. The data indicates that halogenating bowl cleaners cause damage to flapper valve elastomers and result in valve leakage. The tested flappers were either made from a compound of PVC (plasticized polyvinyl chloride) or a compound of an ethylene propylene rubber.

Introducing typical halogenating bowl cleaners (Clorox Automatic® or 2000 Flushes-Bleach®) to the tanks resulted in leakage of some of the flush valves (see Tables 9 and 11 in Appendix C). Introduction of 2000 Flushes-Blue®, a detergent-type bowl cleaner did not induce flapper leakage; it did, however, appear to seal leaks that occurred in two of the 18 flush valves during the course of the 24-week test (see Table 13 in Appendix A).

Microscopic examination of the flappers at the end of the test revealed that leakage could be attributed to warpage and surface roughness of the valves that had been subjected to exposure to the halogenating type of bowl cleaners. The flappers exposed to the detergent type of bowl

cleaner did not become rough and, as mentioned, did not leak after 24 weeks of testing. The results of the durability testing are summarized in the table below and details are provided in Appendix C.

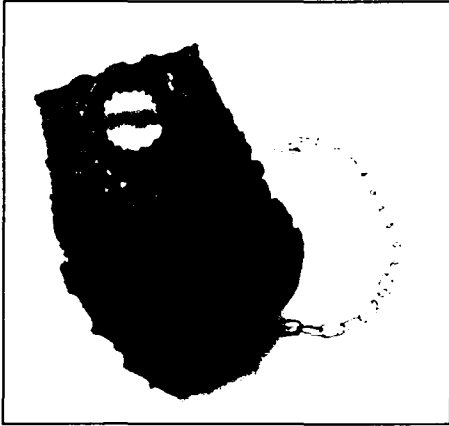
Durability Testing With Bowl Cleaners

	<u>Number of leaking valves at end of 24-week test¹</u>		
<u>Bowl Cleaner/ Valve Material</u>	<u>Clorox Automatic®²</u>	<u>2000 Flushes-Bleach®³</u>	<u>2000 Flushes-Blue®⁴</u>
Ethylene Propylene Rubber Flapper	0	2	0
PVC Flapper	5	4	0

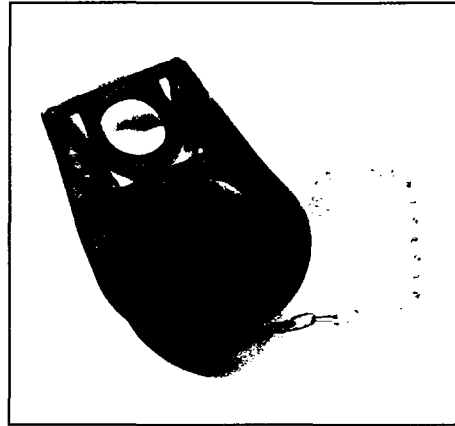
- 1- Leak rate ranged from 5.7 to 11.4 liters per hour. Leakage was due to warping and roughness.
- 2- Halogenating agent type bowl cleaner; total of 18 flappers on 9 ULF toilet models
- 3- Halogenating agent type bowl cleaner; total of 16 flappers on 8 ULF toilet models
- Detergent-type bowl cleaner, total of 18 flappers on 9 ULF toilet models

Figure 3

Typical flapper immersed for 5 months in:



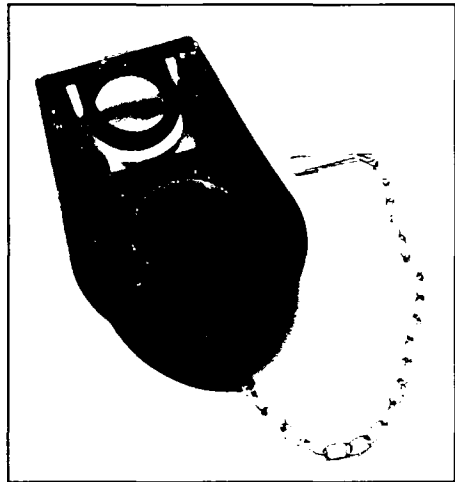
Halongenating Bowl Cleaner "A"



Halongenating Bowl Cleaner "B"



Detergent-type Bowl Cleaner



Municipal Tap Water

RECOMMENDATIONS

Several recommendations follow from the results of the Program as carried out on the flapper valves and rubber compounds that were submitted for testing. To prevent toilet leakage and subsequent water loss due to the chemical attack on rubber parts by halogenating bowl cleaners, one or more of the following approaches should be considered by the manufacturers:

- (a) construct flush valves/flappers of materials impervious to chemical attack;
- (b) develop an alternate flush valve design;
- (c) reduce the chemical concentration of in-tank bowl cleaners; or
- (d) develop a mechanism to introduce the concentrated cleaning chemical directly into the bowl (rather than via the tank water).

In view of these needs, it is specifically recommended that:

Flush Valves

1. Alternate designs be considered by the valve manufacturers that use more impervious materials for the valve and/or the seal contact area. Alternate technologies and/or valve designs that do not depend on traditional flush valves or an elastomeric seal should be explored as well.
2. Testing be carried out on the newer materials used on flappers installed in 1998 products. Metropolitan facilities and services could be made available for testing these newer materials and designs. The recommended tests would be: (a) accelerated immersion testing for weight gain, dimensional changes, and surface microscopy; and (b) durability testing in the environment of today's bowl cleaners. With newer flush valve designs, it will be important to review and amend (as necessary) the testing protocol to anticipate possible changes in the failure modes of the valve and materials.
3. The plumbing industry, through the ASME/ANSI standards process, develop and adopt minimum standards and specifications for flush valves (original equipment and after-market) and other trim parts subject to degradation in various water environments. It is important that these be performance and durability standards and specifications rather than material specifications. This study showed that specifying the type of elastomer in a valve would not necessarily ensure acceptable performance of that valve.

Bowl Cleaners

4. Literature be enclosed (preferably by the toilet manufacturers) in new ULF toilet packaging describing the potential adverse effects of the use of halogenating bowl cleaners. This literature should (a) warn the customer about the consequences of the halogenating bowl cleaners in their new toilet and (b) inform the customer of the need to flush the toilet at least once per day when using these products. Consideration should also be given to a program to

inform all other homeowners of the consequences of using halogenating bowl cleaners in their toilets.

5. Manufacturers explore toilet designs that would provide for storing the bowl cleaner in a separate compartment within (or adjacent to) the toilet that would introduce the bowl cleaner directly into the toilet bowl upon demand. Such a design could isolate the elastomeric materials subject to degradation from the halogenating chemicals.
6. Metropolitan survey customers to determine how many households use halogenating bowl cleaners in order to: (a) estimate the number of real-world flapper valve failures; (b) estimate the water losses resulting from these failures; (c) determine the costs to customers for repair of the failing valves; and (d) design programs that will encourage customers to fix those leaking valves.

Technical Appendix A

Test Protocol

I. Purpose

To test available elastomeric materials in toilet bowl conditions to determine which material would make the best long lasting flapper valve.

II. Scope

This project will test the physical properties of sheet stock material as well as the practical properties of formed flapper valve configurations in both simulated long term "natural environments" and accelerated aging environments.

III. Procedure - Sheet Stock

A. Accelerated Test

1. Test specimens will be ASTM D412 Die "C" dumbbells (dogbones) cut from supplied sheet stock or molded according to these specifications. The specimens will be bent end to end to orient the surface stress across the neck. Five (5) specimens will be required for immersion, plus 5 for initial testing.
2. Test specimens will be inserted circumferentially into screw top jars, one compound per jar. The jar will have a Teflon lined cap and measure approximately 2 1/2 X 4". The closed jar will be kept at 40°C in a well ventilated circulating air oven.
3. Test duration will be a minimum of 30 days. Test solution will be changed daily (except weekends) from a stock solution maintained at 5°C in a refrigerator. The stock solution will be made as needed and will be analyzed initially and at each solution change.
4. There will be various solutions tested. The initial solutions will be a 300 PPM chloramine

solution to give an accelerated look at seasonal water quality parameters and 300 PPM automatic toilet bowl cleaner solutions (mixed halogenated methyl hydantoin type and calcium hypochlorite type) to simulate a build up of one of the more aggressive toilet bowl cleaners.

B. Mechanical Properties Testing

1. Swelling (water absorption)
 - a. A modified ASTM rubber swelling test (ASTM D 412) will be used to determine water absorption. This test is used as a non-destructive means of assessing elastomer degradation.
2. Tensile Properties
 - a. Tensile strength and elongation (stress and strain) will be tested following ASTM D 412. These tests will be performed on the Corrosion Section Instron Model 4206 Universal Testing Machine.
3. Weight gain of specimens will be examined at the end of the test period. This will be achieved by taking an initial weight of the specimen before testing. After the test, the specimen will be pat dried with a lint free cloth and weighed. The specimen will then be placed in an oven maintained at 40 C. The specimen will be removed from the oven and weighed on a periodic basis until it has reached a "constant weight". At this point the final weight will be subtracted from the initial weight and a weight "gain" or "loss" will be reported.
4. An initial and final hardness will be taken (in accordance with ASTM D2240).

5. Surface conditions will be examined by the naked eye and under magnification. These conditions will be evaluated and reported by professionals in the elastomer field.

IV Procedure - Formed Flapper Valve

A. Apparatus Set-Up - Simulated Long Term Aging

1. Actual toilet tanks and stock flapper valves will be used for testing. Flapper valve/tank combinations will be set up as they would be encountered in the real world.
2. There will be 2 racks of tanks plumbed to a control water (at this time it will be finished water from the Weymouth Plant, however, this may change if testing warrants).
3. There will be an air actuated cylinder controlled by an electrically operated solenoid valve to flush each tank. The solenoid valves will be controlled by a computer operated control system capable of varying the flush cycle to any rate desired by the operator.
4. Each tank will be internally marked with a normal fill line. The purpose of the fill line is to indicate a normal or "zero loss" level.

B. Test Parameters - Simulated Long Term Aging

1. The parameters for this test will be as follows:
 - a. The flush cycle will be 1 flush every two minutes. This will last for 5 weeks and result in approximately 25,000 flushes.

- b. At this time a drop-in bowl cleaner will be added to the tank and the flush cycle will be reduced to one flush per week. This will last for 5 weeks.
 - c. At this time the bowl cleaner will be removed and the two minute cycle will resume for two weeks, generating approximately 10,000 flushes.
 - d. At this time the one week cycle will resume with bowl cleaner added for five weeks.
 - e. At this time the bowl cleaner will be removed and the two minute cycle will resume for two weeks, generating approximately 10,000 flushes.
 - f. At this time the one week cycle will resume with bowl cleaner added for five weeks.
- 2. This test would be equivalent to approximately 10 years of flushing at the rate of 12 flushes per day and would include 15 weeks of contact with concentrated bowl cleaner (the concentrations reached when the toilet is not flushed for a week- we call it "vacation time").
 - 3. This test will be performed with bowl cleaners of each type (calcium hypochlorite and halogenated methyl hydantoins) on each variety of flapper valve.

C. Test Monitoring and Evaluation - Simulated Long Term Aging

- 1. Flapper valves will be visually inspected before test begins for cracks, deformation, etc. If any

defects are found it shall be noted or flapper changed if warranted.

2. The tanks will be visually inspected on a weekly basis. It will be noted if tanks are full. If tanks are not full, the amount of fluid loss will be determined by refilling to the fill line using a graduated beaker and noted, along with the amount of stand time and the amount of time the flapper valve has been in service.
3. If the flapper valve has failed, after taking all initial readings as stated in step C-1, the flapper valve will be removed and visually inspected for cracks, deformity, warpage, etc. These findings will be noted.
4. All findings will be correlated with physical properties determined by the accelerated "dogbone" tests.

Technical Appendix B

Material Safety Data Sheets (MSDS)



The Clorox Company
7200 Johnson Drive
Pleasanton, California 94588
Phone: 510-847-6100

Material Safety Data Sheet

I Product: CLOROX AUTOMATIC TOILET BOWL CLEANER														
Description: WHITE TABLET WITH CHLORINE ODOR														
Other Designations	Manufacturer	Emergency Telephone Nos.												
	The Clorox Company 1221 Broadway Oakland, CA 94612	For Medical Emergencies, call Rocky Mountain Poison Center: 1-800-446-1014 For Transportation Emergencies, call Chemtrec: 1-800-424-9300												
II Health Hazard Data		III Hazardous Ingredients												
<p>Direct contact with eyes may cause irreversible damage. Harmful if swallowed. Direct contact with mucous membranes may cause severe irritation or irreversible damage. Severe skin irritant. Prolonged contact with skin may cause irreversible damage.</p> <p>No medical conditions are known to be aggravated by exposure to this product.</p> <p>FIRST AID:</p> <p>EYE CONTACT: Flush eyes immediately with water for at least 15 minutes; then call a physician.</p> <p>INGESTION: Rinse mouth, and drink a glassful of water. Do not induce vomiting. Call a physician.</p> <p>SKIN CONTACT: Wash skin immediately with water for 15 minutes; then call a physician.</p> <p>INHALATION: Remove to fresh air. If irritation or breathing problems persist, call a physician.</p>		<table border="1"><thead><tr><th>Ingredient</th><th>Concentration</th><th>Worker Exposure Limit</th></tr></thead><tbody><tr><td>Bromochloro-5,5-dimethylhydantoin CAS # 126-06-7</td><td>50 - 70%</td><td>Not established.</td></tr><tr><td>1,3-Dichloro-5,5-dimethylhydantoin CAS # 118-52-5</td><td>20 - 40%</td><td>0.2 mg/m³ - TLV-TWA* 0.4 mg/m³ - TLV-STEL^b</td></tr><tr><td>1,3-Dichloro-5-ethyl-5-methylhydantoin CAS # 89415-87-2</td><td>5 - 20%</td><td>Not established.</td></tr></tbody></table> <p>*TLV-TWA = ACGIH Threshold Limit Value - Time Weighted Average. *TLV-STEL = ACGIH Threshold Limit Value - Short-Term Exposure Limit.</p> <p>None of the materials in this product are on the IARC, OSHA, or NTP carcinogen lists.</p>	Ingredient	Concentration	Worker Exposure Limit	Bromochloro-5,5-dimethylhydantoin CAS # 126-06-7	50 - 70%	Not established.	1,3-Dichloro-5,5-dimethylhydantoin CAS # 118-52-5	20 - 40%	0.2 mg/m ³ - TLV-TWA* 0.4 mg/m ³ - TLV-STEL ^b	1,3-Dichloro-5-ethyl-5-methylhydantoin CAS # 89415-87-2	5 - 20%	Not established.
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1,3-Dichloro-5-ethyl-5-methylhydantoin CAS # 89415-87-2	5 - 20%	Not established.												
IV Special Protection and Precautions		V Transportation and Regulatory Data												
<p>Hygienic Practices: Wash hands after direct contact. Do not wear product-contaminated clothing for prolonged periods.</p> <p>Engineering Controls: Not normally required if product is used as directed. However, if handling of product produces dust, local exhaust may be necessary.</p> <p>Personal Protective Equipment: Wear safety glasses or goggles and rubber gloves. Respiratory equipment is not normally required if product is used as directed. However, if handling of product produces dust, respiratory equipment may be necessary.</p>		<p>DOT Proper Shipping Name: Consumer Commodity ORM-D.</p> <p>IMO Proper Shipping Name: Dangerous goods in limited quantities of Class 5.1.</p> <p>IATA Proper Shipping Name: Oxidizing solid, n.o.s., Class 5.1, Packing Group II.</p> <p>EPA - SARA Title III/CERCLA: This product is a hazardous chemical reportable under Sections 311/312; contains no chemicals regulated under Section 313; and contains no chemicals which are regulated under Section 304/CERCLA.</p>												
VI Spill Procedures/Waste Disposal		VII Reactivity Data												
<p>Spill Procedures: Wear appropriate protective gear and respiratory protection. Sweep up material and place in a compatible container for disposal. Since material is toxic to fish, do not discharge into lakes, streams, ponds or public water unless in accordance with NPDES permit.</p> <p>Waste Disposal: Dispose of in accordance with all applicable federal, state, and local regulations.</p>		<p>Reacts with other household chemicals such as acid toilet bowl cleaners, rust removers, acids, vinegar, and ammonia-containing products to produce hazardous gases, such as chlorine/bromine and other chlorinated/brominated compounds. Avoid contact with strong alkalis.</p> <p>Material is an oxidizer. Avoid contact with readily-oxidizable materials.</p> <p>Stable under normal use and storage conditions.</p>												
VIII Fire and Explosion Data		IX Physical Data												
Not flammable or explosive. Decomposes at 165°C. Do not use ABC-type fire extinguishers with fires involving this product.														



BLOCK DRUG COMPANY, INC.

257 Cornelison Avenue Jersey City, N.J. 07302-9988

Telephone (201) 434-3000

MSDS012A

MATERIAL SAFETY DATA SHEET

24 HOUR EMERGENCY CHEMTREC TELEPHONE # (800) 424-9300

DATE PREPARED: August 16, 1991

I. GENERAL INFORMATION

PRODUCT NAME: 2000 Flushes Automatic Bowl Cleaner

PRODUCT CATEGORY: Toilet Bowl Cleaner

II. INGREDIENTS

HAZARDOUS INGREDIENTS:	%	CAS #	TLV	HAZARD DATA:
Calcium Hypochlorite	21-24	7778-54-3	None established	Oxidizer/Corrosive
Calcium Chlorate	0-1.6	10137-74-3	None established	Toxic/Potential Explosive
Calcium Chloride	0-1.6	10043-52-4	None established	Irritant
Calcium Hydroxide	0-1.3	1305-62-0	5mg/m ³	Corrosive
Calcium Carbonate	0-1.3	471-34-1	10mg/m ³	Irritant

III. HEALTH HAZARD DATA

EFFECTS OF OVEREXPOSURE:

INHALATION: Irritating to the nose, mouth, throat, and lungs. May cause respiratory tract irritation with shortness of breath, wheezing, choking or chest pain. Asthma and respiratory and cardiovascular diseases may be aggravated by exposure.

EYES: Can cause severe irritation and/or burns. Direct contact may cause impairment of vision and corneal damage.

SKIN: Can cause severe irritation and/or burns.

INGESTION: Irritation and/or burns due to hypochlorite can occur to the entire gastrointestinal tract, characterized by nausea, vomiting, diarrhea, abdominal pain, bleeding, and/or ulceration. The inert base (marble chips), if ingested by small children, could cause choking by airway obstruction.

This compound is not known or reported to be carcinogenic by IARC, OSHA, NTP or EPA.

FIRST AID PROCEDURE:

EYES: Immediately flush with large amounts of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Call a physician at once.

SKIN: Immediately flush with water for at least 15 minutes. Call a physician. If clothing comes in contact with the product, it should be removed immediately and laundered before reuse.

INGESTION: Immediately drink large quantities of water. Do not induce vomiting. Call a physician at once. Give nothing by mouth if unconscious or having convulsions.

INHALATION: Remove victim to fresh air. Support respiration if needed. Call a physician.

IV. SPECIAL PROTECTION INFORMATION

EYE PROTECTION: Avoid eye contact.

SKIN PROTECTION: Wear protective neoprene or PVC gloves when handling dry container contents.

RESPIRATORY PROTECTION: Avoid breathing dust.

VENTILATION: Use adequate ventilation.

V. FIRE & EXPLOSION HAZARD DATA

FLAMMABLE LIMITS: Non-flammable.

EXTINGUISHING MEDIA: Not applicable.

SPECIAL FIRE FIGHTING PROCEDURES: Use water to cool containers exposed to fire. Do not use dry extinguishers containing ammonium compounds.

UNUSUAL FIRE & EXPLOSION HAZARDS: Wear self-contained breathing apparatus (SCBA), as well as standard fire protective clothing.

VI. ENVIRONMENTAL PROTECTION PROCEDURES

SPILL RESPONSE: Neutralize before disposal. Contact CHEMTREC or manufacturer at 1-800-OLIN-911.

WASTE DISPOSAL METHOD: If this product becomes a waste, it is defined as a hazardous waste under 40 CFR 261 and has the following EPA hazardous waste number: D001.

As a hazardous solid waste, must be disposed of in accordance with local, state, and federal regulations in a permitted hazardous waste treatment, storage and disposal facility.

VII. SPECIAL PRECAUTIONS

HANDLING/STORAGE/TRANSPORTATION: Keep tightly sealed, store in a cool, dry well-ventilated area. Do not store above 52°C (125°F).

VIII. REACTIVITY DATA

STABILITY: Avoid high temperature and humidity.

INCOMPATIBILITY: Acids, other oxidizers, organic materials, nitrogen containing compounds and all corrosive liquids, flammables or combustible materials.

HAZARDOUS DECOMPOSITION PRODUCTS: Chlorine gas

IX. PHYSICAL DATA

BOILING POINT (°F): Not applicable.

SPECIFIC GRAVITY (H₂O=1): Not applicable.

VAPOR PRESSURE (mm Hg): Not applicable.

% VOLATILE BY VOLUME: Not applicable.

VAPOR DENSITY (AIR = 1): Not applicable.

pH: @ 25°C=10.5-11.5 (1% solution)

SOLUBILITY IN WATER: (Granules only) 10% @ 25° with white residue. Decomposition temperature 177°C (350°F).

APPEARANCE & ODOR: White granules in inert marble chip base; chlorine odor.

The information provided in this Material Safety Data sheet has been compiled from our experience and data with similar, commercially available materials and is believed to be accurate. No guarantee of accuracy is made. It is the user's responsibility to determine the suitability of this information for the adoption of necessary safety precautions and disposal procedures.



BLOCK DRUG COMPANY, INC.

257 Cornelison Avenue Jersey City, N.J. 07302-9988

Telephone (201) 434-3000

MSDS006

MATERIAL SAFETY DATA SHEET

24 HOUR EMERGENCY CHEMTREC TELEPHONE # (800) 424-9300

DATE PREPARED: August 16, 1991

I. GENERAL INFORMATION

PRODUCT NAME: 2000 Flushes BLUE Automatic Bowl Cleaner

PRODUCT CATEGORY: Toilet Bowl Cleaner

II. INGREDIENTS

HAZARDOUS INGREDIENTS:	%	CAS #	HAZARD DATA:
Cocamide MEA	35	68140-001	Irritant
Sodium Lauryl Sulfate	19	151-21-3	Irritant
Pine Oil	4	8002-09-3	Irritant

III. HEALTH HAZARD DATA

EFFECTS OF OVEREXPOSURE:

SKIN: May cause irritation.

EYES: May cause irritation.

INHALATION: Not applicable.

INGESTION: May produce gastrointestinal irritation, nausea, vomiting and diarrhea.

FIRST AID PROCEDURE:

SKIN: Flush thoroughly with water, then with soap and water.

EYES: Flush with large amounts of water for 15 minutes while holding eyelids open.

INHALATION: Not applicable.

INGESTION: Drink 2-3 glasses of water. Do not induce vomiting. Do not give liquids if unconscious.

IV. SPECIAL PROTECTION INFORMATION

EYE PROTECTION: Not required.

SKIN PROTECTION: Not required.

RESPIRATORY PROTECTION: Not required.

V. FIRE & EXPLOSION HAZARD DATA

FLAMMABLE LIMITS: Not applicable.

EXTINGUISHING MEDIA: Use water, fog, foam, CO₂, or dry chemical extinguishing media.

SPECIAL FIRE FIGHTING PROCEDURES: None

UNUSUAL FIRE & EXPLOSION HAZARDS: None

VI. ENVIRONMENTAL PROTECTION PROCEDURES

SPILL RESPONSE: Not applicable.

WASTE DISPOSAL METHOD: Not applicable.

VII. SPECIAL PRECAUTIONS

HANDLING/STORAGE/TRANSPORTATION: Avoid skin contact. Store in a cool, dry location away from heat sources.

VIII. REACTIVITY DATA

STABILITY: Stable

INCOMPATIBILITY: Avoid moisture, high temperatures

HAZARDOUS DECOMPOSITION PRODUCTS: Thermal decomposition may produce oxides of carbon, nitrogen and sulfur.

IX. PHYSICAL DATA

BOILING POINT (°F): Not applicable.

SPECIFIC GRAVITY (H₂O=1): Not applicable.

VAPOR PRESSURE (mm Hg): Not available.

% VOLATILE BY VOLUME: Not applicable.

VAPOR DENSITY (AIR = 1): Not available.

pH: Not available.

SOLUBILITY IN WATER: Soluble

APPEARANCE & ODOR: Blue solid with pine odor.

The information provided in this Material Safety Data sheet has been compiled from our experience and data with similar, commercially available materials and is believed to be accurate. No guarantee of accuracy is made. It is the user's responsibility to determine the suitability of this information for the adoption of necessary safety precautions and disposal procedures.

Technical Appendix C

Technical Report

by Dr. Edward N. Kresge

INTRODUCTION

Ultra-low flush (ULF) toilets installation has been a key strategy for the Metropolitan Water District of Southern California (Metropolitan) for promoting water savings. For these savings to continue the ULF toilets must maintain their initial performance. This, in turn, demands that toilet valve flappers do not deteriorate and leak.

The object of the flapper testing program at Metropolitan is to help maximize the leak-free life of the flapper and related seals. Understanding seal failure mechanisms that lead to leakage, developing accelerated testing protocols, and identifying durable materials are all seen as important in meeting the overall objective.

While there can be many causes for flapper valve leakage, chemical attack has been associated with valve failure. Some in-tank bowl cleaners, which contain chlorinating agents can have a pronounced deteriorating effect on flappers. These types of cleaners are widely accepted by the consumer as a means of cleaning the toilet bowl with a minimum of direct contact. In addition, purification chemicals for water systems, although used in much lower concentrations, can also attack flappers and elastomeric seals.

Background

Metropolitan has developed a test facility and protocol for testing the performance and durability of toilet valve flappers. Metropolitan's interest in developing this testing program (Program) is to maintain the water savings available from the retrofit of ULF toilets. ULF toilet retrofit savings are directly affected by the quantity and life of the flapper and seals used to contain water in the toilet tank. Test results and performance comparisons from this test facility will also allow staff to better assess the condition of flappers in existing ULF toilet retrofits and to more effectively target any future replacement programs.

Metropolitan currently has co-participated in approximately one million ULF toilet retrofits and, at one time, funded the purchase of 10,000 to 15,000 ULF toilets per month. The prospect of implementing a comprehensive flapper valve replacement program, even with an effective database of addresses and types of ULF toilets, is at best a very expensive effort with no insurance of actual installation. Comparatively, if an improved flapper is installed by the manufacturer at the time of assembly, costly flapper programs can be avoided or at least delayed and water savings maximized.

Initial efforts to develop the Program included an invitation to representatives of the American National Standards Institute (ANSI), American Water Works Association (AWWA) and interested water utilities to visit Metropolitan's Weymouth Treatment Plant March 31, 1994, for an overview discussion of the Program and a morning tour of

plant facilities. The tour highlighted a 5,000,000 gpd Ozonation Research Plant, state-of-the-art Water Quality Laboratory and Corrosion Laboratory where this Program's test facility is located. At this time an official ANSI meeting was held to discuss the Program and appoint a sub-committee charged with developing a test protocol and minimum performance standard for flappers and related seals. An additional ANSI sub-committee has been formed with the goal of meeting with the manufacturers of toilet bowl cleaners in order to discuss how these cleaners or their method of application may be modified in order to minimize flapper deterioration.

Metropolitan's Corrosion Laboratory performs ongoing tests of the materials used in various phases of water treatment and distribution systems. It is one of the few laboratories dedicated to long term testing, and results from these tests are widely distributed and valued by the water utility industry. The Laboratory has the ability to introduce various water quality levels and types of treated water to this Program not normally available to the manufacturing industry. For this reason, in addition to common goals, it has been possible to enlist the cooperation of the many groups currently participating in the Program.

Chlorine and bromine and other halogenating agents in water are well known to attack most elastomer compounds.¹ Only fluorocarbon rubber exhibits little if any adverse effects on exposure to these reactive chemicals. The effects of chloramines on rubber vulcanizates have been documented in the literature.²

Approach

Tests were developed for elastomer test specimens under accelerated conditions. In addition, a testing facility for long term durability testing of production flapper valves in ULF toilets has been developed by Metropolitan.

Accelerated testing is focused on thermoset rubber and thermoplastic elastomer compounds cut from flat sheet stock or molded to ASTM D412 dumbbell (dogbone) specifications. This test is designed to immerse five sample dumbbells, of one material type per container, in a heated halogenating solution for thirty days. A circulating air oven is used to maintain the containers at 40°C (104°F) for the duration of the test. The solution in the containers is changed daily, from a stock supply, in order to insure a constant concentration of halogenating solution (300 PPM in the chlorine tests). In order to maintain integrity the stock solution is analyzed when it is made up and each time the solution is changed.

¹ K. Nagdi, "Rubber as an Engineering Material" Table 15.1, Hanser Publishers, New York (1993).

² C.L. Simmons and P.P. Evanson, "Effect of the additives in domestic water systems on rubber vulcanizates", *Rubber World*, October 1988, pp. 16-24; S. Reiber, "Investigating the Effects of Chloramines on Elastomer Degradation", *Journal of American Water Works Association*, August 1993, pp. 101-111; S. Reiber, "Chloramine effects on elastomer degradation", *Rubber World*, June 1994, pp. 38-45; S. Reiber, *Chloramine Effects on Distribution System Materials*, AWWA Research Foundation, Denver, 1993.

The long term “natural environments” durability test requires simulating actual household use as closely as possible. For this test it was determined that the average household population in Metropolitan’s service area is 2.8 people and according to a Housing and Urban Development (HUD) study each of these people flush four times per day creating a daily cycle of 12 flushes per day per household (2.8 people/household x 4 flushes/person/day = 11.2 rounded up to 12 flushes/day).

Durability testing without toilet bowl cleaner was conducted to assess the mechanical effectiveness of existing flappers. In this test each ULF toilet was flushed immediately after filling for 25,000 cycles.

In testing with toilet bowl cleaners, the ULF toilets were programmed to simulate the flushing cycles typically experienced in a “guest” bathroom or vacation periods. Long-term durability testing was carried out in the test facility by using the following sequence:

<u>WEEKS</u>	<u>FLUSH CYCLE</u>	<u>CONDITION</u>
5	1 flush / 2 min.	water only
5	1 flush / week	bowl cleaner in tank
2	1 flush / 2 min.	water only
5	1 flush / week	bowl cleaner in tank
2	1 flush / 2 min.	water only
5	1 flush / week	bowl cleaner in tank

In this sequence the flapper valves are in contact with concentrations of toilet bowl cleaner that would build up when a toilet is not flushed for one week (vacation time or periods of non-use in a guest bathroom) for a total time of 15 weeks. The toilets were flushed approximately 45,000 times and represent ten years of flushing at a rate of 12 flushes per day. Details of the test are in Appendix A.

Chlorine Concentration Build-Up

To establish the concentration of chlorine that could build-up in a ULF toilet during non-use periods, a tablet of Clorox-Automatic was placed in 1.6 gallons of tap water and the chlorine concentration measured over a period of time. The following results were obtained:

<u>Time, weeks</u>	<u>Chlorine Conc., PPM</u>
start	-
2	432
14	2312

TESTING

Materials Tested

Rubber compounds potentially useful for the production of flappers were submitted by a number of manufacturers as test specimens for accelerated testing. Sheets or molded test pieces of rubber compounds were submitted by a synthetic rubber manufacturer, a thermoplastic elastomer manufacturer, and several flapper valve manufacturers through contacts at ANSI.

Toilets and flappers for durability and long term testing were obtained from a number of tank suppliers who were also interested in the program.

Table 1 shows the types of materials submitted by suppliers of elastomers and flapper valves. The molded test specimens and valves consisted of various thermoplastic and crosslinkable elastomers. The thermoplastics are processed by injection molding into the final part. The crosslinkable elastomers are process by molding and curing (vulcanization) during a heat cycle.

The thermoplastic materials include thermoplastic elastomers that are based on a crosslinked elastomer phase in a continuous isotactic polypropylene phase by dynamic vulcanization (DVA) technology. Many of the grades of DVA are based on saturated polyolefins, e.g., isotactic polypropylene and ethylene propylene rubber. These polymers are relatively inert to many types of chemical attack and would be expected to perform well under many environments. Plasticized polyvinyl chloride (PVC), which is a thermoplastic was also represented by a number of samples. The PVC backbone is fairly inert to reactions by halogens, but these compounds must be plasticized to be elastomeric. The plasticizers, depending on the type, could readily react with halogenation agents leading to property changes in service. Another thermoplastic material, Styrene-ethylene butene-Styrene tri-block copolymer (S-EB-S), was also submitted. This polymer is produced by hydrogenation of styrene-butadiene-styrene block copolymer. If there is any unsaturation remaining in the polymer backbone after hydrogenation there will be a site for chemical attack. As with all of the thermoplastic polymers other compounding ingredients could be subject to reaction or extraction during testing.

The crosslinkable elastomers included in the test are both saturated backbone hydrocarbon polymer and should be fairly inert. Ethylene propylene rubber (EPR) used as a thermoset and when used to produce a DVA may have side-chain unsaturation that is used for crosslinking. The polyisobutylene based copolymer also has a reactive site for vulcanization but has a saturated polymer backbone and is typically inert to chemical attack. The rubber compounds also contain potentially reactive or extractable materials which could lead to property changes on contact with halogenating agents. Additionally, depending on the specific crosslinking chemistry, the crosslinks in the rubber network could be broken by halogenation leading to a rapid deterioration in physical properties.

As indicated in the Table, some polymer types were determined by discussion and/or literature from the suppliers. Other polymer types were determined by infra-red analysis performed by Akron Rubber Development Laboratory, Inc. Akron, Ohio using a standard ASTM method. Only the types of polymers were determined. Other materials in the compound, such as, plasticizers, fillers, curatives, etc. were not determined. While these compounding are clearly critical to durability performance, their influence is much beyond the scope of the current study.

The Material Safety Data Sheets for the toilet bowl cleaners are in Appendix B. These data sheets indicate that the Clorox material is a mixture of 1,3-bromo- and 1,3-dichloro-5,5-dimethylhydantoin and 1,3-dichloro-5-ethyl-5-methylhydantoin. The 2000 Flushes is mainly calcium hypochlorite. Supplies of the bowl cleaners were obtained from retail distributors and used without modification.

Accelerated testing

For accelerated testing dumbbells were cut from sheet stock or molded and inserted circumferentially in a 2 ½ inch diameter jar containing the halogenating solution. Temperature was maintained at 40°C. Details of the procedure are in Appendix A.

After exposure the samples were examined for surface appearance, cracks at rest, and cracks at 50% extension under 30x magnification. The samples were also cut and the appearance of the cross-section were examined at 30x. Surface tack was measured as well as the ease of surface erosion. Changes in hardness and stress-strain properties were measured by standard rubber testing methods before and after exposure as was the percent weight change after exposure while wet and then fully dried. The types of tests and relationship to potential failure in flappers are listed in Table 2.

Results of the accelerated testing in chloramine solution, Clorox Bowl Cleaner, and 2000 Flushes-White are shown in Tables 3-8.

Durability Testing of Flapper Valves

Durability Testing without Bowl Cleaners present

During the durability test set-up for flapper valves no particular installation problems were encountered, instruction sheets were clear and assembly went well for all units. Preliminary dye tablet tests at the time of installation showed that both WC tanks were leaking one drop every 5 seconds. Initial static inspection (no flush sequence) showed that the WC flappers were slightly warped as installed. After ten days of testing the upper bank WC tank had stopped leaking while the lower bank WC continued to leak, draining the tank within ten minutes. After 32 more days, this tank had stopped leaking as well. Apparently during this time both flappers were able to comply

with the seat well enough to form a satisfactory seal. None of the other tanks showed any leakage for the full duration of the test. The only other event was a broken flush arm on the upper Toto which was replaced with a generic metal arm. A summary of the daily log of events is given in Appendix Table 1.

Durability Testing with Bowl Cleaners

Long term testing of flapper valves with bowl cleaners was carried out as detailed in Appendix A. The bowl cleaners were introduced into the tanks and the flush cycle was operated once in every seven days. This flush cycle frequency was done to simulate a typical household away on vacation or the “Guest” bathroom which is not frequently used. During the periods of no flushing the “drop-in -additives” increased in concentration as they would under this type of usage. Leak tests were done on a weekly basis over the test period and after test completion all of the flappers were evaluated for damage that could or did lead to leakage.

Evaluations of the exposed flapper valves after durability testing included how easy or difficult it was to erode the surface exposed to the tank water by scraping, how much warpage there was in the seat area of the valve, cracking on extension, and roughness of the exposed surface (See Table 2). The drain-side surface of the valve, which is only in contact with the tank water during the flush cycle, was also examined for roughness or other deterioration.

The results for the long term durability testing with bowl cleaners are presented for Clorox Drop-In, 2000 Flushes-white and 2000 Flushes-Blue in Tables 9-11.

RESULTS AND DISCUSSION

Prediction of Long Term Durability

The first step in the durability assessment of flapper valves is defining the types of failure mechanisms that limit service life. In general, all materials can be sensitive to the temperatures, fluids, chemicals, and mechanical conditions they encounter in actual service. Rubbers, in particular, can undergo property changes large enough to contribute to failure. Rubber compounds vary widely in their resistance to specific environments depending on the type of rubber, fillers, plasticizers, stabilizers, crosslinking agents, and other compounding ingredients. Property changes brought about by chemical reactions in combination with mechanical conditions (fluid swelling, flexing, straining, abrasion) are largely responsible for failures of elastomeric parts while in service.

If the failure mechanism(s) can be isolated for a rubber part, then it is usually possible to predict long term durability by using appropriate testing methods. The testing can often be accelerated by increasing concentrations of reactants, increasing the test

temperature, or increasing the mechanical severity as long as changing the conditions do not change the failure mechanism. The response to reactive chemical concentration effects, activation energies of reaction, and changes in mechanical severity must all be quantified. Activation energies are of particular concern because of the change in reaction rate with temperature can be specific to the exact type of reaction and /or reaction conditions. In this study to date we have limited our work to determining possible failure mechanisms.

Possible Failure Mechanisms

Toilet flapper valves could fail and leak by a number of different mechanisms. The failure could be due to abrasion , seal surface deterioration, cracking, changes in dimension or shape or other means. All of the mechanisms can be altered by the environment (temperature, chemical reactions) and by the type of material used in the flapper valve.

Flapper valve sealing materials or the entire valve assembly are most frequently manufactured from an elastomer (either thermoset or thermoplastic). As pointed out, most polymers are not inert to halogenating agents and the chemical attack of these agents on the rubbers degrade physical properties and cause dimensional changes that are critical for effective sealing.

Halogenating agents attack rubber either on the polymer network chains or on the crosslinks between the chains if they are thermoset materials. These reactions, by changing the nature of the rubber network can cause significant changes in physical properties. Halogenating agents can also attack plasticizers and other ingredients that are used in elastomer compounds. Chloramine is a halogenating agent and the N-H could be reactive as well by other reaction mechanisms. (For example, failure of automotive engine seals, made from the fluorocarbon elastomer Viton, resulted from amine attack on the small amount of C-H and C-S bonds in the polymer to form more crosslinks. The amines are part of the additive package in engine oil. The added crosslinks made the polymer brittle and the seals failed.)

Depending on the type of halogenating agent, concentration and type of rubber, the reactions are usually diffusion controlled. This means that the attack begins on the surface and progresses toward the interior of the material when the rubber is in the unstrained state. When the rubber is strained, usually above some critical strain value, the chemical attack can cause cracking in the material. (This is most commonly observed as cracking of rubber bands when they are stretched in air that contains low concentrations of ozone.) The critical strains needed for crack formation in elastomers due to chemical attack can be quite low, around 1 % strain. This strain level is likely experienced by elastomers in some valve types when the valve is closed and, for a very short time, when the valve is opened.

Surface reactions lead to surface erosion when the valve is in service and can cause leakage by abrasion or transfer of valve material to the valve seat. Dimensional changes caused by swelling, shrinkage or warping are usually related to attack on the interior of the valve material.

Another possible valve failure mechanism could be related to flex fatigue. In this case, repeated flexing or straining of the valve could result in crack growth and subsequent failure. This is a common mechanism of failure in many rubber parts in dynamic application (shoe soles, drive belts, automotive tires) and is highly influenced by flexing conditions.³

Accelerated Testing

Exposure to Chloramine

Exposure of molded elastomer test specimens to 300 PPM chloramine for 30 days results in significant property changes as shown in Table 3. The wt. % swell ranged from 11 to over 90 % and all samples exhibited a drop in hardness ranging from 2 to about 20 points Shore A. The smaller hardness losses would not be expected to change sealing characteristics. In fact, somewhat lower hardness could provide for a tighter seal because of better conformity to the seat. Larger changes in hardness, however, indicate major damage to the elastomeric network. Stress-strain properties also reflect attack by the chloramine on either the polymer backbone or the crosslinks. Lavell-4 and Mansfield DG, which were determined to be based on ethylene-propylene rubber or an ethylene-propylene-diene rubber (EPR), showed the smallest changes in both weight swell and physical properties. Mansfield BK, which was also determined to be an EPR, however, had a high weight swell and drastic changes in physical properties. This illustrates the importance of other compounding materials besides the base elastomer in determining changes in properties when contacted with chloramine. Mansfield LG, a PVC based compound, and two of the thermoplastic elastomer samples (J and K), based on DVA technology, also showed relatively low swell and minimum changes in other properties.

Microscopic examination of the test specimens at 30X, Table 4, were consistent in most cases with the changes observed in swell and physical properties. Higher swells, in general, resulted in rougher surfaces after exposure and sample distortion. The type of elastomer also contributed to the type of damage caused by chloramine. The test samples based on S-EB-S (Lavell-2 and 3) were found to have cracks before or after extension. These cracks were on the strained side of the test specimen. As mentioned previously, this is similar to the observation of unsaturated elastomers exposed to ozone, where cracks will only grow if the material is strained above some small but critical value. The PVC based sample, Mansfield LG, had minimum changes in physical properties, but microscopic examination after exposure revealed a rough surface with blisters and an interior having numerous large pores. The rough surface and blisters, in particular,

³ M.D. Ellul, Chapter 6, *Engineering with Rubber*, A.N. Gent, ed., Hanser Publishers, New York, 1992.

suggest a potential for poor sealing characteristics. The low swelling DVA (J and K) compounds were highly distorted. The high percent weight gain after exposure suggests considerable reaction with the chloramine had taken place. The EPR based test specimens microscopic examination were in line with the changes in physical properties and were also dependant on the detailed nature of the compounding ingredients. The isobutylene copolymer based samples all had tacky surfaces after exposure while the interior of the specimens appeared to be unchanged. This suggests that any reactions that are taking place are restricted by diffusion of the reactants. This is consistent with the low diffusion rates for small molecules in polyisobutylene based elastomers. It is not clear how a tacky surface would alter sealing ability of a flapper valve, but it could conceivably lead to operability problems due to sticking.

An important observation is that samples that have high weight swell also are highly distorted. The distortion could cause the valve to not seat properly and result in leakage. Additionally, samples with large losses in physical properties are also easily eroded by scraping and erosion in service could also cause leakage in a flapper valve.

Exposure to Clorox Drop-In

On exposure to Clorox Drop-In for 30 days at 40°C. all seventeen rubber samples showed some change in both physical properties and microscopic examination, Tables 5 and 6. In general, under these test conditions contact with Clorox Drop-In (mainly a mixture of bromochloro-5,5 dimethylhydantoin and dichloro-5,5 dimethylhydantoin) appears to be more aggressive than chloramine in attacking some flapper compounds. As with the chloramine exposure, there is a correspondence between the physical property changes and the microscopic examination of the samples. Usually, samples that exhibited the largest changes in hardness, swell, and stress-strain properties showed the largest changes in surface characteristics and distortion that are expected to degrade flapper seal performance.

Property changes were minimal with Lavell-4 based on an EPR compound and while the surface became moderately tacky it was smooth. Low swell, low tack and a smooth surface was also experienced by the Mansfield DG based on EPR, however, tensile strength dropped to about one-half of the original value.

The PVC sample represented by Mansfield LG retained its physical properties but had a high wt. % swell. Microscopic examination disclosed an extremely rough surface, cracking, a hard layer, interior porosity, and a high degree of distortion.

Lavell-3 (S-EB-S) had 15 wt. % swell and good physical property retention, while Lavell-2 (also S-EB-S) had 39 wt. % swell. Microscopic examination showed blisters, cracks, and tack. Lavell-2 also had many water filled voids and was soft and spongy.

The DVAs had variable changes in physical properties. Samples J and K had the lowest swells and fair property retention, but K had a rough surface and J was slightly rough.

The polyisobutylene polymers exhibited moderate swell and good physical property retention. The surfaces were very tacky and there was a gummy layer that could be removed, suggesting that the surface has lost its crosslinks and is no longer a network. For this exposure time the depth of the layer was about 1/10 the thickness of the sample.

Exposure to 2000 Flushes White

As with the chloramine and Clorox Drop-In, for 2000 Flushes White (mainly calcium hypochlorite) there was a correlation with changes in physical properties and microscopic observations of the test samples, Tables 7 and 8. Stress-strain properties deteriorated as well. Many samples lost significant tensile strength and failed at shorter elongations; in some cases tensile strengths dropped by up to 1/3 of the original values as did elongations at failure.

Lavell-4 (EPR) demonstrated the best performance with a swell of 9.5 wt. %. Physical properties were retained for the most part and microscopic examination showed a smooth surface, low tack and no cracking. The surface (about 1/10) of the sample became yellow while the interior remained orange. The EPR based Mansfield samples exhibited higher swells and larger loss in properties. While the surface of the Mansfield DG (EPR) was similar to the Lavell-4, the Mansfield BK (also EPR) showed considerable degradation with pits, roughness, cracks, and large scale distortion.

The Mansfield LG (PVC compound) retained physicals, but microscopic examination revealed a very rough surface with countless water filled blisters. Moreover, the test piece was highly distorted and had a highly eroded surface layer. Lavell-2 (S-EB-S) had a rough surface and the cross section showed many water filled voids.

The DVAs responded to exposure to 2000 Flushes White in a manner quite similar to Clorox Drop-In. There were variable changes in physical properties, swell and surface characteristics. Samples J and K had the lowest swells and fair property retention, but K had a rough surface that could be scraped off and J was slightly rough.

The polyisobutylene type polymers had moderate swell and a diffusion controlled attack on the surface. Unlike the other chemicals, 2000 Flushes White did not cause these sample to become tacky. The surfaces were white and water could be expressed from the outer layer of the sample, suggesting a loss of crosslinks on exposure.

Effects of Halogenating Agents

In general, exposure to chloramine and the tested toilet bowl cleaners results in major changes in elastomer compounds. In many cases, depending on the length of

exposure and concentration, these changes would be expected to contribute to actual physical failure of flappers or to cause leakage by distortion, surface erosion, or other means. Under the test conditions, there was no clear indication that a specific type of halogenating agent was the most aggressive in attacking all of the different rubber compounds.

After exposure to halogenating agents weight percent swell ranged from a low of 9.2% to 61%. Depending on the design of the flapper valve made from these materials, these changes in physical dimensions due to swelling could lead to sealing problems, particularly for high degrees of swelling. Swelling can cause poor fit and/or distortion of the valve causing leaks. It should be noted that two different types of swelling are observed for these test samples. In some samples there is an overall uniform swelling of the compound and in others the swelling also involves blister and internal void formation. For samples which exhibited the void and blistered formation, pressing or cutting of the samples caused considerable water expression. These types of samples also tended to have very rough and/or blistered surfaces that would clearly result in sealing limitations.

Dry weights after exposure and drying to constant weight were used to determine percent weight gain or loss. The weight changes reflect loss or gain of material, e.g., possible loss of plasticizer or chlorine addition reactions. It is also possible that the overall weight changes reflect some combination of weight gain and weight loss. Weight loss was as high as 16 percent and weight gain as high as 23 percent in the case of chloramine accelerated testing. The changes were more modest with the toilet bowl cleaners, but are nevertheless still significant also suggest that halogenation reactions are taking place with the rubber compounds. Since the weight gains or losses in some cases are found to be quite different for rubber compounds with the same basic polymer, polymer selection alone will not predict performance during exposure.

Exposure resulted in crack formation on some of the test compounds. As would be expected from crack formation, this also resulted in very low tensile strength and low elongation to failure due to stress concentration at crack tips. Cracks could prove to be problematic in flapper valves by initiation of crack growth failure and/or leakage at crack sites.

Examination of cross-sections of the exposed test pieces indicate that for many of the materials the damage is diffusion controlled. Damage is greatest at the surface and the interior having no apparent damage, with a boundary between the damaged and undamaged areas. For the amount of exposure experienced for these samples, the damage had progressed for about 1/10 to 1/4 the thickness of the sample. The finding that some samples are diffusion controlled and some are not is important for further testing and prediction of service life. This is because samples with diffusion controlled damage will behave in fundamentally different ways than samples where damage is controlled by a different mechanism (usually different temperature and concentration responses and failure modes).

Durability Testing with Bowl Cleaners

Flapper valves from nine different suppliers were tested for long term durability as outlined in Appendix I. Runs 24 weeks in length were carried out in duplicate and three different bowl cleaners were used; Clorox Automatic, 2000 Flushes-White, and 2000 Flushes-Blue. According to the MSDS information, 2000 Flushes-Blue is 35% Cocamide MEA and 19% sodium lauryl sulfate. Unlike the Clorox and 2000 Flushes-White products, the 2000 Flushes-Blue is not a halogenation agent.

As shown in Table 1, the analysis of eight of the flapper valves indicated that they were produced from either EPR or PVC. The valves that were analyzed were valves that had been subject to durability testing with the 2000 Flushes-Blue. Since this bowl cleaner should not be reactive with most materials, it was possible to determine the types of polymers that were used in the compounds. The Toto valve was not submitted for analysis because we had no sample.

Durability Testing with Clorox Automatic

Table 9 presents the leak rates for the nine different valves with Clorox Automatic Bowl Cleaner. Five types of valves showed no leakage during the full 24 week test period, one sample of one valve leaked on an intermittent basis, and for another valve the duplicates performed differently. None of the EPR based flapper valves leaked during the test. The PVC based valves the results were mixed. In the valves that leaked, the water loss rate was very substantial by the end of the test, ranging from 6 to 11 liters/hour.

Examination of the valves after the durability test showed an excellent correlation between leakage and the condition of the valve (Table 10). Warp and roughness of the surface exposed to the water containing the bowl cleaner appeared to account for the leakage. None of the valves showed any cracking on extension, suggesting that cracking is not a typical mechanism for valve failure when using these types of compounds.

Durability Testing with 2000 Flushes-White

Table 11 gives the results of durability testing with 2000 Flushes-White bowl cleaner. In this case, only three of the eight valves were not leaking at the end of the test period. One of the two EPR based valves leaked. One-half of the PVC based valves also leaked. In contrast to the Clorox exposure, the leaks with the 2000 Flushes-White appeared to show up in the later stages of the test (~week 22 vs. ~week 8). Actual leak rates (5.5 to 6.6 liters/hour) were also not quite as high for the 2000 Flushes-White as for the Clorox Bowl Cleaner. Again warp and surface roughness (Table 12) appeared to be the cause of the leaks and no cracking in the valves was observed after the test was completed.

Durability Testing with 2000 Flushes-Blue

In contrast to the halogenating bowl cleaners, 2000 Flushes-Blue durability testing produced no leaks after 24 weeks (Table 13). In this testing sequence two of the valves showed some leakage at the start of the test, but no leaks at the end. Table 14 indicates that only the Lower W.C. was slightly rough at the termination of the test and that all of the other valves were smooth and exhibited either no or only slight warpage. Additionally, the valve surfaces were covered with slimy coating. This soft coating could actually improve valve seating and correct of any surface roughness, thereby minimizing any leakage.

In comparing the durability testing with all three types of bowl cleaners, the type of polymer (PVC or EPR) in the valve did not appear to be a determining factor. This finding is consistent with the data from the accelerated exposure testing which indicate that polymer type alone does not establish performance. Other compounding ingredients, fillers, plasticizers, curatives, etc., all appear to play a major role in flapper valve performance.

CONCLUSIONS

Halogenating agents (chloramine, hypochlorite, halohydantoins) interact adversely with most materials used for elastomeric seals in toilet flapper valves. At the high concentrations of hypochlorite and halohydantoins that might be realistically expected when using a toilet bowl cleaner in the tank, many flapper valves fail due to this interaction within 24 weeks of testing. Considerable amounts of water can be wasted through the leaking of flapper valves unless they are promptly replaced and the use of halogenating bowl cleaners is discontinued.

Seal failure appears to be primarily associated with swelling, distortion and surface roughening due to chemical attack of the elastomeric compound. The more complex failure mechanisms observed in other elastomer applications, such as dynamic cut-growth, strain induced cracking, catastrophic mechanical failure, abrasive wear, etc., were not observed in our durability testing. The swelling, distortion and surface roughening is generally associated with the formation of water filled voids within the rubber compound rather than a uniform total mass increase due to halogenation reactions.

The accelerated tests and flapper valve durability tests were carried out on 18 different compounds. The polymer elastomeric backbones represented included saturated hydrocarbons (ethylene propylene copolymer, isobutylene copolymer, ethylene butene copolymer, polypropylene) and polyvinylchloride. All of these polymer backbones would be expected to be attacked by halogenating agents at a relatively slow rate under the exposure conditions. The wide variation among samples produced using the same backbone polymer emphasizes the criticality of other compounding ingredients

(fillers, plasticizers, crosslinking agents, etc.). This indicates that toilet flapper valves cannot be specified by polymer backbone material alone and that performance specifications are required for the compounds.

The accelerated tests developed in this study appear to be a good screening tool for flapper valve materials. Since seal failures are mostly associated with distortion and surface deterioration, the wt. % swell and microscopic examination of the testing are the most important aspects. Changes in stress-strain properties after exposure are generally consistent with the wt. % swell and microscopy. Large changes in stress-strain properties might help predict mechanical failure for some valve designs.

The development of accelerated tests to reliably predict the expected service life of flapper valves will require considerable effort. The effects of halogenating agent concentration, temperature, diffusion control, and other variables would be expected to change with the specific chemical reactions involved and therefore with specific compound ingredients. This means that different rubber compounds might respond quite differently to increased temperature and concentration as a means to accelerate degradation and there will be no single predictive relationship for all compounds that allows extrapolation to predicted service life.

RECOMMENDATIONS

Several recommendations follow from the results of the testing carried out on flapper valves and rubber compounds submitted. To prevent toilet leakage and subsequent water loss due to the chemical attack on rubber parts by halogenating bowl cleaners, either the flapper valves must be constructed of materials impervious to such attack or the concentration of the cleaners must be greatly reduced or eliminated.

The only elastomers largely impervious to attack by chlorine in water appear to be fluorocarbon rubbers (e.g. Viton™ and Fluorel™). These are very costly materials and flappers of the current designs that are constructed totally of rubber would be highly expensive. Therefore, it is recommended that alternate designs be considered that use alternate materials for the valve and/or the seal contact area. Alternate technologies that do not depend on an elastomeric seal should be explored as well.

Additional testing of materials is also needed. The idea would be to test newer materials and designs that are provided by original equipment and after-market manufacturers. Metropolitan facilities and services could be made available for testing these products. Based on this study the appropriate tests are: (a) accelerated immersion testing for weight gain, dimensional changes and surface microscopy; and (b) durability testing in the environment of bowl cleaners. With newer designs it will be important to review the testing protocol to anticipate possible changes in failure modes.

This study shows that very harsh chemical environments exist in some toilet tanks. The industry should develop and adopt minimum standards and specifications for

flapper valves and other rubber parts relating to degradation in various water environments. It is important that these be performance and durability standards and specification rather than material specifications. For rubbers that are currently used in flapper valves, we found that specifying the type of elastomer in a valve would not insure performance.

There are many flapper valves in place that are rapidly degraded by halogenating bowl cleaners. The use of these type of cleaners, particularly if the toilet is not flushed often, will likely result in premature flapper failure and subsequent water loss. It is recommended that literature be enclosed in ULF toilet packages on the dangerous bowl cleaners. This literature should warn the customer against the use of these products and the requirement to flush at least once per day if, for some reason, they are going to use such a product. Consideration should also be given for a program to inform users of existing toilets about the consequences of using these bowl cleaners.

To establish the extent of the problem, it is recommended that Metropolitan survey customers to determine how many households use halogenating bowl cleaners (e.g. 2000 Flushes-White and Chlorox Automatic or similar products). In addition to determining the extent of penetration of these products in the Metropolitan service area, it may be possible to construct the survey to estimate the number of flapper valve failures. This information could help establish not only water loss rates, but also repair costs to customers associated with the halogenating bowl cleaners.

Table 1 Types of Elastomers / Polymers Tested

<u>Sample</u>	<u>Composition of Sample</u>	<u>Note</u>
<u>Molded Test Specimens</u>		
DVA “B”	Thermoplastic elastomer based on DVA technology	1
DVA “F”	Thermoplastic elastomer based on DVA technology	1
DVA “J”	Thermoplastic elastomer based on DVA technology	1
DVA “K”	Thermoplastic elastomer based on DVA technology	1
DVA “N”	Thermoplastic elastomer based on DVA technology	1
DVA “P”	Thermoplastic elastomer based on DVA technology	1
LG	Plasticized Polyvinyl Chloride	2
BK	Ethylene Propylene Rubber	2
DG	Ethylene Propylene Rubber	2
L-1	-	3
L-2	Styrene-Ethylene/Butene-Styrene thermoplastic elastomer	2
L-3	Styrene-Ethylene/Butene-Styrene thermoplastic elastomer	2
L-4	Ethylene Propylene Rubber	2
E-2	Isobutylene copolymer rubber	1
E-4	Isobutylene copolymer rubber	1
E-5	Isobutylene copolymer rubber	1
E-7	Isobutylene copolymer rubber	1
<u>Flapper Valves</u>		
St Thomas	Plasticized Polyvinyl Chloride	2
Mansfield	Ethylene Propylene Rubber	2
Briggs	Plasticized Polyvinyl Chloride	2
W. C.	Plasticized Polyvinyl Chloride	2
Eljer	Plasticized Polyvinyl Chloride	2
Toto	-	3
American Std	Ethylene Propylene Rubber	2
Kohler	Plasticized Polyvinyl Chloride	2
Crane	Plasticized Polyvinyl Chloride	2

Notes

1. Type of polymer based on literature and discussions with sample supplier
2. Polymer type determined for this study by ASTM D 3677-90 (1995) using a Perkin Elmer 1760 FTIR Spectrometer and samples prepared by film or pyrolysis method depending on the thermoplasticity of the material
3. No data

Table 2
Evaluations of Samples Subjected to Accelerated Testing

<u>Tests/Observations</u>	<u>Relationship to potential seal failure</u>
Surface appearance at 30x	Surface changes (pits, blisters, roughness) that could cause leakage
Cracks at rest at 30x	Possible leakage and failure points
Cracks at 50% extension at 30x	Check for internal sample damage and failure points
Cross-section at 30x	Relative amount of surface and internal changes, diffusion control of reactions
Surface tack	Indication of surface reactions and sealing problems
Surface erosion	The ability of the surface to withstand erosion by scraping; combination of chemical attack and abrasion seal failures
Wet swollen weight gain	Seal failure due to dimensional instability
Dry weight after water removal	Check of rubber and/or plasticizer loss
Hardness	Changes in physical characteristics related to sealing
Stress-strain properties	Changes that could lead to physical failure of flapper valves

Table 3 Property Changes After Exposure to Chloramine

<u>Sample</u>	<u>Swelling and Weight-Loss</u>		<u>Hardness</u>		<u>Stress-Strain Properties, Initial/Exposed</u>		
	<u>Wt. % Swell</u>	<u>Wt. % change</u>	<u>Shore A</u>		<u>50% Modulus</u>	<u>Tensile Strength</u>	<u>% Elongation</u>
DVA "B"	25	2.7	68	59	270/240	1030/580	420/200
DVA "F"	61	1.1	79	68	400/440	1390/730	300/100
DVA "J"	16	11.3	84	77	540/570	1670/940	470/220
DVA "K"	24	23.3	84	74	520/520	1310/860	380/180
DVA "N"	36	3.0	74	60	180/150	560/430	240/210
DVA "P"	93	-16.0	57	48	360/450	1070/870	200/100
LG	12	8.9	79	73	530/530	1170/1180	280/280
BK	43	-.8	76	75	660/N/A	2090/650	160/50
DG	10	2.6	61	60	170/170	1240/760	730/560
L-1	14	.5	32	29	70/70	620/520	520/410
L-2	26	1.0	35	28	80/80	420/390	410/380
L-3	20	6.1	38	29	150/130	330/330	450/690
L-4	11	3.4	39	35	50/50	no break/680	680/650
E-2	41	-.7			90/60	1040/1430	400/440
E-4	53	1.7			80/80	540/830	270/420
E-5	45	1.3			60/60	1620/1220	500/520
E-7	58	.5			60/60	1410/990	680/630

**TABLE 4 MICROSCOPIC OBSERVATIONS (30X) AFTER EXPOSURE TO 300 PPM
CHLORAMINE**

SAMPLE #	TACK	SURFACE APPEARANCE	CRACKS (NO EXTENSION)	CRACKS AT 50% EXTENSION	SURFACE EROSION	CROSS SECTION	REMARKS
DVA "B"	none	slightly rough	none	none	none	uniform, dense, more lightening on surface	
DVA "F"	none	smooth	none	none	very slight	smooth interior	highly distorted
DVA "J"	none	rough, blisters on surface	none	none	slight	smooth interior, slight rind effect	stiff, highly blistered at gate mark, highly distorted
DVA "K"	none	very rough, blistered	none	none	moderate	smooth interior, slight surface effect	highly distorted
DVA "N"	slight	smooth	none	none	none	smooth, slight line effects	
DVA "P"	slight	slightly rough	none	none (some water expression	none	smooth no apparent skin effect. Water expression	highly distorted
L.G.	none	rough - blisters both sides	none	none	none	uniform - has numerous large pores	
B.K.	very slightly	smooth with deep pock marks	none	none	crumb scrapes off	uniformly, with hard skin effect	extremely swollen, highly distorted
D.G.	none	smooth	none	no cracks, no water	none	very slight skin effect	

TABLE 4 CONTINUED							
SAMPLE #	TACK	SURFACE APPEARANCE	CRACKS (NO EXTENSION)	CRACKS AT 50% EXTENSION	SURFACE EROSION	CROSS SECTION	REMARKS
L- 1	slight	smooth with blistered areas	none	one side only	none	uniform	water erosion on one side
L- 2	slight	smooth	cracks- one side	cracks	none	surface attack	water expression on extension
L- 3	slight	smooth	strain-induced cracks	strain-induced cracks	none	uniform, smooth	internal damage, water release on extension
L- 4	none	smooth	none	none	none	uniform, smooth	
E- 2	very	roughened	none	no change	scrapes off sticky layer	thin damaged surface	no interior damage
E- 4	very	smooth	none	large eroded areas with water expression	sticky layer scrapes off	see remarks	surface damage, interior O.K.
E- 5	very	rough	none	large eroded areas	light sticky layer comes off	see remarks	surface damage, interior O.K.
E- 7	very	slightly roughened	none	none	sticky layer scrapes off	surface damage only	no water expression

Table 5 Property Changes After Exposure to Clorox Drop-In

<u>Sample</u>	<u>Swelling and Weight-Loss</u>		<u>Hardness</u>		<u>Stress-Strain Properties, Initial/Exposed</u>		
	<u>Wt. % Swell</u>	<u>Wt. % change</u>	<u>Initial</u>	<u>Exposed</u>	<u>50% Modulus</u>	<u>Tensile Strength</u>	<u>% Elongation</u>
DVA "B"	56	16	67	56	410/360	1010/510	400/170
DVA "F"	24	4.4	78	73	620/640	1420/1020	300/200
DVA "J"	15	2.8	84	77	470/500	720/580	200/100
DVA "K"	16	2.3	83	76	500/560	520/1140	60/280
DVA "N"	N/A	N/A	57	47	190/190	625/500	250/210
DVA "P"	31	0.9	74	66	650/630	1000/900	170/140
LG	45	0.2	78	62	690/750	1120/1090	210/190
BK	36	4.0	75	68	880/N/A	2110/850	190/90
DG	11	0.6	62	58	280/250	1190/490	730/390
L-1	25	0.8	31	20	100/70	560/440	490/580
L-2	39	1.6	35	24	125/100	370/340	360/410
L-3	15	2.5	40	24	75/50	310/350	410/490
L-4	9.2	-0.1	38	34	50/80	880/710	640/660
E-2	18	2.2	40	32	120/120	1080/1100	400/440
E-4	20	2.4	39	32	75/75	670/930	300/420
E-5	22	2.0	38	30	80/80	1370/1630	460/540
E-7	22	2.3	38	26	no break	no break	no break

TABLE 6 MICROSCOPIC OBSERVATIONS (30X) AFTER EXPOSURE TO CLOROX
DROP IN BOWL CLEANER

SAMPLE #	TACK	SURFACE APPEARANCE	CRACKS (NO EXTENSION)	CRACKS AT 50% EXTENSION	SURFACE EROSION	CROSS SECTION	REMARKS
DVA "B"	none	smooth	none	none	none	white skin 1/4 in, light yellow interior	sample distorted
DVA "F"	none	smooth	none	none	none	uniform	fairly stiff sample
DVA "J"	none	very slightly rough	none	none	none	uniform	
DVA "K"	none	rough	none	none	very thin surface layer can be scraped off	uniform	surface layer is some type of thin polymer film
DVA "N"	very	some surface blisters	none	none	gummy layer chunks off	no discernible skin	
DVA "P"	slight	rough surface	none	none	none	small voids throughout sample	water is expressed when scraping surface
L.G.	none	extremely rough	some cracking	some cracking	hard layer scrapes off	small open pores; some large open pores; diffuse skin	sample highly distorted and swollen
B.K.	none	very rough and many large blisters	none	none	hard layer easily scrapes off	large water-filled voids 1/5 in	sample distorted and swollen
D.G.	none	smooth	none	none	none	outer layer 1/10 in separated from core by a thin white layer	

TABLE 6 CONTINUED							
SAMPLE #	TACK	SURFACE APPEARANCE	CRACKS (NO EXTENSION)	CRACKS AT 50% EXTENSION	SURFACE EROSION	CROSS SECTION	REMARKS
L- 1	very	rough with many large water-filled blisters	none	none	slight with water expression	large water-filled voids under a surface skin	sample highly swollen
L- 2	moderate +	rough with large water- filled blisters	some	some	none	many water-filled voids	soft and spongy
L- 3	slight	gummy coating; blisters	slight cracking on 1 side only	cracks	some	white surface skin, lighter diffusion area 1/10 in	
L- 4	moderate	smooth	none	none	none	orange interior, yellow skin 1/4 in	
E- 2	very	smooth	none	none	gummy layer removed	very thin white surface layer	surface has lost network
E- 4	very	smooth	none	none	gummy layer removed	white surface layer < 1/10 in	surface has lost network
E- 5	very	slightly rough	none	none	gummy layer removed	white surface layer < 1/10 in	surface has lost network
E- 7	very	smooth	none	none	gummy layer removed	white surface layer < 1/10 in	surface has lost network

Table 7 Property Changes After Exposure to 2000 Flushes-White

<u>Sample</u>	<u>Swelling and Weight-Loss</u>		<u>Hardness</u>		<u>Stress-Strain Properties, Initial/Exposed</u>		
	<u>Wt. % Swell</u>	<u>Wt. % change</u>	<u>Initial</u>	<u>Exposed</u>	<u>50% Modulus</u>	<u>Tensile Strength</u>	<u>% Elongation</u>
DVA "B"	50	1.0	68	52	300 / 250	970 / 650	400 / 220
DVA "F"	26	-0.6	79	72	430 / 480	1500 / 1100	320 / 200
DVA "J"	16	2.6	82	77	740 / 500	1990 / 620	470 / 110
DVA "K"	24	2.5	81	73	580 / 510	1520 / 550	390 / 60
DVA "N"	38	2.0	56	44	190 / 125	620 / 360	250 / 210
DVA "P"	27	-3.8	75	56	440 / 420	1080 / 775	190 / 120
LG	37	0.4	77	62	550 / 590	1160 / 1070	260 / 180
BK	30	1.9	72	55	460 / 710	2460 / 790	210 / 70
DG	16	-0.8	61	58	170 / 170	1170 / 620	710 / 440
L-1	27	0.9	33	24	65 / 50	540 / 260	460 / 390
L-2	37	1.6	36	24	85 / 75	390 / 190	390 / 270
L-3	19	2.4	38	36	125 / 125	300 / 470	390 / 770
L-4	9.5	-1.5	40	32	55 / 55	960 / 660	600 / 660
E-2	13	-1.3	41	32	90 / 90	1020 / 750	380 / 410
E-4	25	0.9	40	33	90 / 60	780 / 730	350 / 390
E-5	20	1.2	38	30	50 / 65	1380 / 1180	480 / 490
E-7	24	-0.6	40	28	90 /	1330 / no break	670 /

TABLE 8 MICROSCOPIC OBSERVATIONS (30X) AFTER EXPOSURE TO 2000
FLUSHES WHITE PRODUCT

SAMPLE #	TACK	SURFACE APPEARANCE	CRACKS (NO EXTENSION)	CRACKS AT 50% EXTENSION	SURFACE EROSION	CROSS SECTION	REMARKS
DVA "B"	none	smooth	none	none	none	white skin 1/4 in, light yellow interior	sample distorted
DVA "F"	none	smooth	none	none	none	uniform	fairly stiff sample
DVA "J"	none	very slightly rough	none	none	none	uniform	
DVA "K"	none	rough	none	none	very thin surface layer can be scraped off	uniform	surface layer is some type of thin polymer film
DVA "N"	slight	smooth	none	none	some surface erosion and water expression	white layer 1/4 in, light white interior	
DVA "P"	none	rough water-filled blisters	none	none	water expression on scraping	thin skin 1/10 in is voided, interior dense	
B.K.	none	very rough surface, numerous pits	none	sample broke at < 50%, numerous cracks	considerable surface erosion with water expression	skin 1/6 in, uniformly black	sample highly distorted, went from gray to white after exposure
D.G.	none	smooth	none	none	none	uniform and dense	no color change from control
L.G.	none	extremely rough and countless water-filled blisters	none	none	surface erosion and considerable water expression	highly eroded surface layer, many small interior pores with pores surrounded by yellow	sample highly distorted and very stiff

TABLE 8 CONTINUED							
SAMPLE #	TACK	SURFACE APPEARANCE	CRACKS (NO EXTENSION)	CRACKS AT 50% EXTENSION	SURFACE EROSION	CROSS SECTION	REMARKS
L-1	slight	rough	few	few	some surface erosion with considerable water expression	small water-filled voids	swollen
L-2	slight	slightly rough	none	some	slight surface erosion with considerable water expression	many small water-filled voids	swollen
L-3	none	a few tiny water- filled blisters	none	none	none	slightly whitened 1/10 in	
L-4	none	smooth	none	none	none	bright orange interior, yellow skin 1/10 in	unexposed sample is red/orange
E-2	none	slight roughness	none	none	no surface erosion, but slight water expression	white surface 1/10 in, light straw interior	slight water in surface only
E-4	none	smooth	none	none	moderate surface erosion with water expression	white surface layer 1/8 in, yellow interior	water in surface only
E-5	none	smooth	none	none	very slight surface erosion with slight water expression	white surface layer 1/8 in, straw-colored interior	water in surface only
E-7	none	smooth	none	none	no surface erosion, but water expression	white surface layer 1/10 in, off white interior	water in surface only

NOTES FOR TABLES 4, 6, AND 8 MICROSCOPIC EXAMINATION OF EXPOSED SAMPLES

1. All observations were made with a stereomicroscope at 30x magnification with incident light.
2. The estimation of tack are indicated as follows:

<u>Level of tack</u>	<u>Description</u>
none	dry, non-tacky surface
slight	small amount of tack
moderate	about like a "Post-it Note"
very	approaching the tack of Scotch tape

3. Surface erosion was measured by scraping with a new single edge razor blade held at a right angle to the rubber surface with moderate pressure.
4. A sharp needle probe was used to examine any blisters to ascertain if they contained water.

TABLE 9 DURABILITY TEST WITH CLOROX AUTOMATIC BOWL CLEANER

LEAK RATES IN LITERS/HOUR

	MANSFIELD	TOTO	BRIGGS	ELJER	W.C.	CRANE	AMER. STD.	ST. THOMAS	KOHLER	COMMENTS
	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	
INITIAL INSPECTION	0 / 0	0 / 0	0 / 0	0 / 0	.72 / .72	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 1	0 / 0	0 / 0	0 / 0	0 / 0	0 / 6.1	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 2	0 / 0	0 / 0	0 / 0	0 / 0	0 / 6.1	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 3	0 / 0	0 / 0	0 / 0	0 / 0	0 / 1	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 4	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 5	0 / 0	0 / 0	0 / 0	0 / 0	0 / 4	0 / 0	0 / 0	0 / 0	0 / 0	ADD BOWL CLEANER. REDUCE FLUSH
WEEK 6	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	CYCLE TO 1X PER WEEK.
WEEK 7	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
WEEK 8	0 / 0	0 / 0	11.4 / 11.4	0 / 0	15 / 6.1	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 9	0 / 0	22.8 / 0	22.8 / 22.8	0 / 0	6.1 / 6.1	1.0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 10	0 / 0	0 / 0	0 / 0	0 / 0	6.1 / 1	1.0 / 0	0 / 0	0 / 0	0 / 0	REMOVE BOWL CLEANER. RETURN CYCLE
WEEK 11	0 / 0	0 / 0	11.4 / 11.4	0 / 0	6.1 / 1	11.4 / 0	0 / 0	0 / 0	0 / 0	TO EVERY 2 MINUTES.
WEEK 12	0 / 0	0 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	ADD BOWL CLEANER. REDUCE FLUSH
WEEK 13	0 / 0	0 / 0	11.4 / 11.4	0 / 0	6.1 / 3.05	11.4 / 0	0 / 0	0 / 0	0 / 0	CYCLE TO 1X PER WEEK.
WEEK 14	0 / 0	11.4 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	
WEEK 15	0 / 0	0 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	
WEEK 16	0 / 0	11.4 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	
WEEK 17	0 / 0	11.4 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	REMOVE BOWL CLEANER. RETURN CYCLE
WEEK 18	0 / 0	11.4 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	TO EVERY 2 MINUTES.
WEEK 19	0 / 0	0 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	ADD BOWL CLEANER. REDUCE FLUSH
WEEK 20	0 / 0	0 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	CYCLE TO 1X PER WEEK.
WEEK 21	0 / 0	0 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	
WEEK 22	0 / 0	0 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	
WEEK 23	0 / 0	0 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	
WEEK 24	0 / 0	0 / 0	11.4 / 11.4	0 / 0	6.1 / 6.1	11.4 / 0	0 / 0	0 / 0	0 / 0	

TABLE 10 EXPOSED FLAPPER VALVE EVALUATIONS
CLOROX AUTOMATIC BOWL CLEANER

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SAMPLE	WARPAGE ²	EXPOSED SURFACE ⁴	EXPOSED SURFACE EROSION ³	DRAIN SIDE SURFACE ⁴	CRACKING ON EXTENSION ⁵	OTHER REMARKS
LOWER ST THOMAS ¹	+	ROUGH ++	NONE	SMOOTH	NO	
UPPER ST THOMAS ¹	+	ROUGH ++	NONE	SMOOTH	NO	
LOWER MANSFIELD ¹	SLIGHT	SMOOTH	NONE	SMOOTH	NO	
UPPER MANSFIELD ¹	NONE	SMOOTH	NONE	SMOOTH	NO	
LOWER BRIGGS	++++	ROUGH ++++	+++	ROUGH ++	NO	
UPPER BRIGGS	++++	ROUGH ++++	+++	ROUGH ++	NO	
LOWER W.C.	+++	ROUGH ++++	+++	ROUGH +	NO	
UPPER W.C.	++++	ROUGH ++++	+++	ROUGH +	NO	
LOWER ELJER	NONE	SMOOTH	NONE	SMOOTH	NO	PART LIGHTER GREEN ON DRAIN SIDE
UPPER ELJER	NONE	SMOOTH	NONE	SMOOTH	NO	
LOWER TOTO	NONE	SMOOTH	NONE	SMOOTH	NO	APPEARS SIMILAR TO ELJER
UPPER TOTO ¹	+	ROUGH ++	+	SMOOTH	NO	APPEARS SIMILAR TO AMERICAN STANDARD

TABLE 10
CONTINUED

LOWER AMERICAN STANDARD ¹	+	ROUGH ++	+	SMOOTH	NO	
UPPER AMERICAN STANDARD ¹	+	ROUGH ++	+	SMOOTH	NO	
LOWER KOHLER ¹	+	ROUGH ++	+	SMOOTH	NO	APPEARS SIMILAR TO AMERICAN STANDARD
UPPER KOHLER ¹	+	ROUGH ++	+	SMOOTH	NO	APPEARS SIMILAR TO AMERICAN STANDARD
LOWER CRANE	NONE	SMOOTH	NONE	SMOOTH	NO	SLIGHT YELLOWING AROUND SEAL AREA
UPPER CRANE	++++	++++	++	ROUGH ++	NO	WHITE EXUDATION ON TOP SURFACE

¹ Rubber seal area examined-- two-part valve.

² Relative amount of distortion from having a flat seal area

³ Surface physical property loss which could lead to erosion as determined by scraping with razor blade

⁴ Relative surface roughness by examination at 10X magnification

⁵ Extension to 50% and 10X magnification for cracks

TABLE 11 DURABILITY TEST WITH 2000 FLUSHES-WHITE BOWL CLEANER

LEAK RATES IN LITERS/HOUR

	MANSFIELD	TOTO	BRIGGS	ELJER	W.C.	CRANE	AMER. STD.	ST. THOMAS	KOHLER	COMMENTS
	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	
INITIAL INSPECTION	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 1	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 2	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 3	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 4	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 5	0 / 0	0 / 0	0 / 0	0 / 0	N/A	3 / 0	0 / 0	0 / 0	0 / 0	*ADD BOWL CLEANER REDUCE FLUSH
WEEK 6	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	CYCLE TO 1X PER WEEK
WEEK 7	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 8	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 9	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 10	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	*REMOVE BOWL CLEANER RETURN CYCLE
WEEK 11	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	TO EVERY 2 MINUTES
WEEK 12	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	*ADD BOWL CLEANER REDUCE FLUSH
WEEK 13	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	CYCLE TO 1X PER WEEK
WEEK 14	0 / 0	0 / 0	0 / 0	0 / 0	N/A	9 / 0	0 / 0	0 / 0	0 / 0	
WEEK 15	0 / 0	0 / 0	0 / 0	0 / 0	N/A	48 / 0	0 / 0	0 / 0	0 / 0	
WEEK 16	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 17	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	*REMOVE BOWL CLEANER RETURN CYCLE
WEEK 18	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	TO EVERY 2 MINUTES
WEEK 19	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	*ADD BOWL CLEANER REDUCE FLUSH
WEEK 20	0 / 0	0 / 0	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	CYCLE TO 1X PER WEEK
WEEK 21	0 / 0	0 / 57	0 / 0	0 / 0	N/A	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 22	0 / 0	0 / 0	0 / 0	0 / 37	N/A	0 / 0	19 / 0	44 / 0	0 / 0	
WEEK 23	0 / 0	0 / 0	0 / 1	0 / 37	N/A	38 / 0	38 / 1	44 / 0	0 / 0	
WEEK 24	0 / 0	0 / 0	0 / 57	0 / 55	N/A	57 / 0	57 / 57	66 / 0	0 / 0	

NOTE: FLAPPERS WERE NOT AVAILABLE FOR W.C. - IT WAS NOT TESTED THIS TIME. FLAPPERS SUPPLIED FOR ST. THOMAS WERE NOT EXACTLY THE SAME AS PREVIOUS TESTS

TABLE 12 EXPOSED FLAPPER VALVE EVALUATIONS
2000 FLUSHES-WHITE

SAMPLE	EXPOSED SURFACE EROSION ³	WARPAGE ⁴	EXPOSED SURFACE ⁵	DRAIN SIDE SURFACE ⁵	CRACK- ING ON EXTEN- SION ⁶	OTHER REMARKS
LOWER ST THOMAS	NONE	SLIGHT	SMOOTH	SMOOTH	NO	
UPPER ST THOMAS	++	++++	ROUGH++++	SMOOTH	NO	
LOWER MANSFIELD ¹	NONE	+	SMOOTH	SMOOTH	NO	EROSION/INDENTATION AT VALVE SEAT
UPPER MANSFIELD ¹	+	+	SMOOTH	SMOOTH	NO	EROSION/INDENTATION AT VALVE SEAT
LOWER BRIGGS	+++	++++	ROUGH++++	SMOOTH	NO	
UPPER BRIGGS	+	+	ROUGH+	SMOOTH	NO	
LOWER ELJER	++	++++	ROUGH++++	SMOOTH	NO	
UPPER ELJER	+	NONE	ROUGH+	SMOOTH	NO	VALVE SEAT SMOOTHER THAN EXPOSED SURFACE AND INDENTED SLIGHTLY
LOWER TOTO	++	++	ROUGH+	SMOOTH	NO	SEAT AREA SLIGHTLY INDENTED
UPPER TOTO	++	+	SMOOTH	SMOOTH	NO	SEAT IS SMOOTHER THAN SURROUNDING AREA

TABLE 12
CONTINUED

LOWER AMERICAN STANDARD ²	+	++++	ROUGH++++	SMOOTH	NO	
2000-FLUSHES WHITE EXPOSURE, CONTINUED						
UPPER AMERICAN STANDARD ²	NONE	++++	ROUGH+++	SMOOTH	NO	SURFACE IS HARD
LOWER KOHLER ²	NONE	NONE	SMOOTH	SMOOTH	NO	SLIGHT SMOOTH DEPRESSION AT THE VALVE SEAT
UPPER KOHLER ²	+++	++++	ROUGH++	SMOOTH	NO	
LOWER CRANE	NONE	+	SMOOTH	SMOOTH	NO	
UPPER CRANE	+	++++	ROUGH++++	SMOOTH	NO	

¹ Flexible valve seat only.

² Rubber seal area examined-- two-part valve.

³ Surface physical property loss which could lead to erosion as determined by scraping with razor blade

⁴ Relative amount of distortion from having a flat seal area

⁵ Relative surface roughness by examination at 10X magnification

⁶ Extension to 50% and 10X magnification for cracks

TABLE 13 DURABILITY TEST WITH 2000 FLUSHES-BLUE BOWL CLEANER

LEAK RATES IN LITERS/HOUR

	MANSFIELD	TOTO	BRIGGS	ELJER	W.C.	CRANE	AMER. STD.	ST. THOMAS	KOHLER	COMMENTS
	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	UPPER/LOWER	
INITIAL INSPECTION	0 / 0	0 / 0	0 / 0	0 / 0	0 / 2.5	1 / 0	0 / 0	0 / 0	0 / 0	
WEEK 1	0 / 0	0 / 0	0 / 0	0 / 0	0 / 2.5	1 / 0	0 / 0	0 / 0	0 / 0	
WEEK 2	0 / 0	0 / 0	0 / 0	0 / 0	0 / 3	1 / 0	0 / 0	0 / 0	0 / 0	
WEEK 3	0 / 0	0 / 0	0 / 0	0 / 0	0 / 3	1 / 0	0 / 0	0 / 0	0 / 0	
WEEK 4	0 / 0	0 / 0	0 / 0	0 / 0	0 / 2.5	.7 / 0	0 / 0	0 / 0	0 / 0	
WEEK 5	0 / 0	0 / 0	0 / 0	0 / 0	0 / 4.1	.7 / 0	0 / 0	0 / 0	0 / 0	*ADD BOWL CLEANER. REDUCE FLUSH
WEEK 6	0 / 0	0 / 0	0 / 0	0 / 0	0 / 6.1	0 / 0	0 / 0	0 / 0	0 / 0	CYCLE TO 1X PER WEEK.
WEEK 7	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	.7 / 0	0 / 0	0 / 0	0 / 0	
WEEK 8	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 9	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 10	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	*REMOVE BOWL CLEANER. RETURN CYCLE
WEEK 11	0 / 0	0 / 0	0 / 0	0 / 0	0 / 3.05	.35 / 0	0 / 0	0 / 0	0 / 0	TO EVERY 2 MINUTES.
WEEK 12	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	*ADD BOWL CLEANER. REDUCE FLUSH
WEEK 13	0 / 0	0 / 0	0 / 0	0 / 0	0 / .5	.5 / 0	0 / 0	0 / 0	0 / 0	CYCLE TO 1X PER WEEK.
WEEK 14	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 15	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 16	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 17	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	*REMOVE BOWL CLEANER. RETURN CYCLE
WEEK 18	0 / 0	0 / 0	0 / 0	0 / 0	0 / 1	0 / 0	0 / 0	0 / 0	0 / 0	TO EVERY 2 MINUTES.
WEEK 19	0 / 0	0 / 0	0 / 0	0 / 0	0 / .75	.25 / 0	0 / 0	0 / 0	0 / 0	*ADD BOWL CLEANER. REDUCE FLUSH
WEEK 20	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	CYCLE TO 1X PER WEEK.
WEEK 21	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 22	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 23	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	
WEEK 24	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	0 / 0	*END OF TEST. ALL FLAPPERS HAD SLIMY COATING, BUT WERE IN GOOD SHAPE.

TABLE 14 EXPOSED FLAPPER VALVE EVALUATIONS
2000 FLUSHES-BLUE

SAMPLE	WARPAGE ²	EXPOSED SURFACE ⁴	EXPOSED SURFACE EROSION ³	DRAIN SIDE SURFACE ⁴	CRACK- ING ON EXTEN- SION ⁵	OTHER REMARKS
LOWER ST THOMAS ¹	SLIGHT	SMOOTH	NONE	SMOOTH	NO	COVERED WITH A SLIGHTLY SLIMY WHITE COATING
UPPER ST THOMAS ¹	SLIGHT	SMOOTH	NONE	SMOOTH	NO	COVERED WITH A SLIGHTLY SLIMY BLuish COATING
LOWER MANSFIELD ¹	SLIGHT	SMOOTH	NONE	SMOOTH	NO	COVERED WITH A SLIGHTLY SLIMY COATING
UPPER MANSFIELD ¹	+	SMOOTH	NONE	SMOOTH	NO	COVERED WITH A SLIGHTLY SLIMY COATING
LOWER BRIGGS	SLIGHT	SMOOTH	NONE	SMOOTH	NO	INDENTATION FROM THE SEAT
UPPER BRIGGS	NONE	SMOOTH	NONE	SMOOTH	NO	INDENTATION FROM THE SEAT
LOWER W.C. ⁶	SLIGHT	SLIGHTLY ROUGH	+	SMOOTH	NO	COVERED WITH GUMMY LAYER; INDENTATION FROM THE SEAT
UPPER W.C. ⁶	NONE	MOLDED IN ROUGHNESS	NONE	SMOOTH	NO	
LOWER ELJER	++	SMOOTH	NONE	MOLDED IN ROUGHNESS	NO	COVERED WITH A SLIGHTLY SLIMY COATING
UPPER ELJER	SLIGHT	SMOOTH	NONE	SMOOTH	NO	COVERED WITH A SLIGHTLY SLIMY COATING

TABLE 14
CONTINUED

LOWER TOTO	NONE	SMOOTH	NONE	SMOOTH	NO	INDENTATION FROM THE SEAT
UPPER TOTO	SLIGHT	SMOOTH	NONE	SMOOTH	NO	INDENTATION FROM THE SEAT
LOWER AMERICAN STANDARD ¹	NONE	SMOOTH	NONE	SMOOTH	NO	
UPPER AMERICAN STANDARD ¹	NONE	SMOOTH	NONE	SMOOTH	NO	
LOWER KOHLER ¹	NONE	SMOOTH	NONE	SMOOTH	NO	SLIGHT IMPRESSION FROM THE SEAT
UPPER KOHLER ¹	NONE	SMOOTH	NONE	SMOOTH	NO	SLIGHT IMPRESSION FROM THE SEAT
LOWER CRANE	SLIGHT	SMOOTH	NONE	SMOOTH	NO	COVERED WITH A SLIGHTLY SLIMY COATING
UPPER CRANE	SLIGHT	SMOOTH	NONE	SMOOTH	NO	COVERED WITH A SLIGHTLY SLIMY COATING

¹ Rubber seal area examined-- two-part valve.

² Relative amount of distortion from having a flat seal area

³ Surface physical property loss which could lead to erosion as determined by scraping with razor blade

⁴ Relative surface roughness by examination at 10X magnification

⁵ Extension to 50% and 10X magnification for cracks

⁶ Molded-in ridge on seal surface from mold parting line

Appendix Table 1
Durability Test Log Book

Date (1995)	Brand Name	Upper/Lower	Comments
June 19	WC	Both	1 drop/5 sec. Leak at assembly
June 26	WC	Upper Lower	1 drop/5 sec. continued leak Drained tank in ten minutes
July 5	WC WC	Upper Lower	Leak stopped Drained tank in ten minutes
July 10	WC	Lower	Leakage reduced to 1 liter/hour
July 17	Toto	Upper	No leaks Flush arm broke

Technical Appendix D

Dr. Edward N. Kresge

Appendix D

Edward N. Kresge Biography

Ed Kresge received his Ph.D. in organic chemistry from the University of Florida and joined the Exploratory Polymers Group of Exxon Chemical Company in 1961. His technical activities at Exxon included research on many polymeric resins, graft copolymers, viscosity modifiers, butyl rubber, ethylene propylene rubber, polymer blends and thermoplastic elastomers. Aspects of this research led to the development and commercialization of several new resins, major grades of ethylene propylene rubber, shear-stable viscosity modifiers for oil, and a successful thermoplastic elastomers joint-venture. He was named the Chief Polymer Scientist for Exxon Chemical Company in 1979 and jointly in 1988 began serving as the Polymer Science Area Leader for Exxon Research and Engineering Company. He has some 45 US patents and his recent publication activity is on polymer blends and thermoplastic elastomers. He retired from Exxon in 1993 and is presently a consultant on polymers.

Along with his individual research contributions and involvement with major team efforts to develop new products and processes, Dr. Kresge had the responsibility for organizing the long range polymer research activity within Exxon Chemical Company, an activity he led for several years. This research activity resulted in major innovations in metallocene catalysis for polyolefin production. In addition, he led teams that established new methods in both the chemicals and petroleum business to achieve innovation, particularly major innovation, from exploratory research through commercialization. As Chief Scientist he was responsible for technology input into strategic planning for Exxon's polymer business and he participated in numerous business studies on polymeric products (adhesives, composites, elastomers, thermoplastic elastomers, thermoplastic resins, etc.)

Dr. Kresge received the Melvin Mooney Technical Achievement Award from the American Chemical Society (ACS) in 1995. Previously, in 1993, the Rubber Division bestowed upon him the Arnold Smith Award. He was a recipient of the National Inventors Hall of Fame Medal in 1976. He served as Chairman of the 1987 Elastomers Gordon Research Conference and was General Secretary of the ACS Macromolecular Secretariat in 1993. He has been a Councilor, Rubber Division, ACS, from 1980 to the present and has served on many National ACS Committees. He is presently on the ACS Society Committee for Professional Training. Dr. Kresge was chair of the Editorial Board of *Rubber Reviews* and on the Editorial Board of *Polymer-Plastics Technology and Engineering*. He has served on ACS Divisional Committees, and chaired several Symposia for the Rubber Division and the ACS including a Symposium on Innovation. He chaired the University of Florida Chemical Industrial Review Board, served on the University of Connecticut Materials Science Board, and was on the Advisory Board for Polymer Science at Massachusetts Institute of Technology.

Technical Appendix E

Samples Submitted for Testing

APPENDIX E

Samples Submitted for Testing

Submitted by	Sample Identification	Form of Sample	No. of Samples
Hoov-R-Line	Black	Flapper	1
Hoov-R-Line	Black "A"	Flapper	1
Hoov-R-Line	Clear	Flapper	1
Hoov-R-Line	Clear "B"	Flapper	1
Hoov-R-Line	Blue	Flapper	1
Hoov-R-Line	Blue "C"	Flapper	1
Mansfield Plumbing Products	211	Flush Valves	4
Mansfield Plumbing Products	None	Circular Seals	20
Mansfield Plumbing Products	DG-Seal	Sheet	2 - 8"x24"
Mansfield Plumbing Products	LG-Vinyl	Sheet	2 - 8"x24"
Mansfield Plumbing Products	BK-Ballcock	Sheet	2 - 8"x24"
Advanced Elastomer Systems	"B"	Dumbbells	20
Advanced Elastomer Systems	"F"	Dumbbells	20
Advanced Elastomer Systems	"J"	Dumbbells	20
Advanced Elastomer Systems	"K"	Dumbbells	20
Advanced Elastomer Systems	"N"	Dumbbells	20
Advanced Elastomer Systems	"P"	Dumbbells	20
Coast Foundry & Manufacturing	No. 400	Flush Valve	4
Coast Foundry & Manufacturing	None	Flapper	40
Frugal Technologies, Inc.	Retroflapper	Flapper	3
Lavelle Industries, Inc.	#1	Flapper	10
Lavelle Industries, Inc.	#1	Dumbbell	60
Lavelle Industries, Inc.	#2	Flapper	10
Lavelle Industries, Inc.	#2	Dumbbell	60
Lavelle Industries, Inc.	#3	Flapper	10
Lavelle Industries, Inc.	#3	Dumbbell	60
Lavelle Industries, Inc.	#4	Flapper	10
Lavelle Industries, Inc.	#4	Dumbbell	60
Exxon Chemical Company	9502011-2	Sheet (pad)	7 - 6"x6"
Exxon Chemical Company	9502011-4	Sheet (pad)	7 - 6"x6"
Exxon Chemical Company	9502011-5	Sheet (pad)	7 - 6"x6"
Exxon Chemical Company	9502011-7	Sheet (pad)	7 - 6"x6"