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Halogen-vapor transmission

Apparatus and method for measuring performance of barrier materials against chlorine and iodine, with data on several useful laminations

Storage stability or shelf life has long been a military problem when a supply of items such as disinfectants must be kept on hand for long periods of time for emergency use. Consistent with the problem of storage stability of disinfectants is adequacy of packaging materials and their ability to protect package contents when stored in military warehouses under extremes of climatic conditions. The packaging material must prevent the entrance of moisture into the contents of the package and at the same time be resistant to attack by disinfectant vapors. The packaging material must also act as a barrier to halogen vapors.

Typifying this problem for halogen-type disinfectants is Disinfectant, Chlorine, Food Service, Specification MIL-D-11309A. This chlorine-releasing disinfectant is composed of chlormelamine, a surface-active material, and a buffer system of citric acid and monosodium dihydrogen phosphate. It is used for rinsing mess gear where 180 deg. F. water is unavailable for the purpose of sanitizing and as a germicidal rinse for fresh fruits and vegetables of questionable origin which are to be eaten raw.

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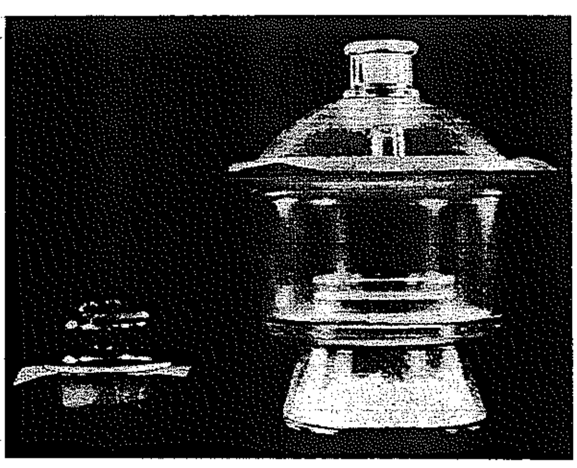
Figure 1. Test cells used to determine halogen-vapor transmission through various packaging materials. Large desiccator (right) is first type of cell used; at left is small, improved test cell.



A laminate structure which is currently used for the packaging of Disinfectant, Chlorine, Food Service, is (from inside to outside) 25 lbs. polyethylene, 0.0035 aluminum foil, 15 lbs. polyethylene, 25 lbs. pouch paper, with a lacquer coating. A heat-sealed pouch made of this laminate for packaging Disinfectant, Chlorine, Food Service, provides only six months' protection of its contents when stored under temperate climatic conditions. After six months' storage, visible pitting and crazing of the pouch is noticeable. This breakdown in the packaging material subsequently permits a loss in the active halogen present in the disinfectant formulation. Thus, a search for a halogen-resistant, pouch-type packaging material which would give considerably longer shelf life than that structure was begun.

A simple and reproducible method for determining chlorine and iodine vapor transmission was required to evaluate candidate packaging materials. The adaptation of the principles used in determining organic-vapor transmission through packaging materials seemed ideal for this purpose.

Cherepow(1)[1] described a method for comparing the flavor or odor permeability of flexible materials using a 4-oz. Douglas jar known as the Cherepow cell. A cross section is cut through a Douglas jar, creating two chambers. The odorous material is placed in the bottom chamber and the test sample is interposed between this and the top chamber. At suitable time intervals the screw cap is removed briefly, the top chamber sniffed, the screw cap quickly replaced and the time required for the first detectable appearance of the odor in the top chamber is recorded. Cartwright, et al.,(2) also used the Cherepow cell in their studies of odor permeability of glassine.

[1] Numbers in parentheses identify References appended.

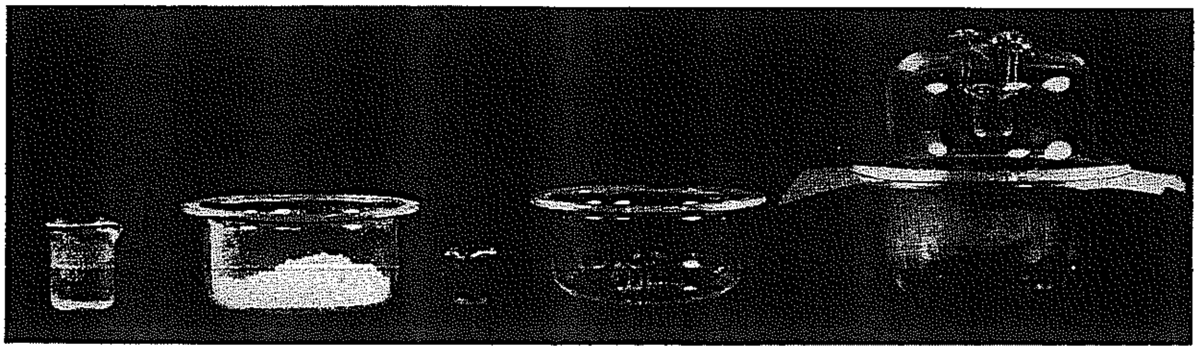


Figure 2. Improved test cell is shown assembled, at right, with sample in place for an iodine-vapor test. To the left are disassembled component parts in preparation for a chlorine-vapor test.

Muldoon, et al.,(3) described a method using a test cell to evaluate organic-vapor transmission, instead of the less reliable organoleptic methods, which is subject to human error and fatigue. This method consisted of two 125-mm. crystallizing dishes, one inverted on top of the other, with the test sample mounted between the two chambers. When assembled for testing, a small Petri dish containing a volatile organic liquid—methyl furoate—is mounted in the center of the top crystallizing dish. A solution of potassium hydroxide is placed in the bottom dish and the specimen to be tested is mounted between the two dishes. The methyl furoate volatilizes, diffuses through the test specimen and is saponified. The amount of furoic acid in the potassium hydroxide solution is measured in a spectrophotometer, since the optical density varies directly with the concentration of furoic acid.

Experimental

The first type of cell used to evaluate various candidate packaging materials in this study is shown in Figure 1. It consists of an ordinary laboratory desiccator with an opening in the lid to take a stopper. A wire hook mounted from the stopper in the lid is positioned so as to permit a 5-ml. beaker containing halogen indicator to hang from it. The halogen releasing disinfectant (Disinfectant, Chlorine, Food Service, used as the source of chlorine, or the standard iodine water purification tablet, Specification MIL-T-283C used as the source of iodine) is placed in the bottom of the desiccator and a Petri dish of water placed on the desiccator shelf. This procedure produces approximately 100% relative humidity conditions within the bottom half of the desiccator, which causes the rapid release of the halogen present in the disinfectant under test.

When assembled for testing, the beaker is half filled with a starch-potassium iodine solution. The lower half of the desiccator contains the disinfectant and Petri dish of water, and the specimen to be tested is mounted between the lid and bottom half of the desiccator. During storage at 37 deg. C., the halogen-containing disinfectant releases either chlorine or iodine (whichever the case may be). The halogen vapors eventually diffuse through the test specimen and react with the starch-potassium iodide indicator. The number of days required for the starch-potassium iodide solution to turn blue is considered the relative resistance of the specimen under test to either iodine or chlorine vapors.

A modification of the test cell under discussion was later undertaken to permit the testing of smaller sample specimens and to permit a larger number of tests to be conducted at a single time. This was made possible by reducing the improved test cell by four to five times the size of the desiccator-type test cell. Figure 1 shows the comparison in size between the two test cells.

The improved test cell is illustrated in detail in Figure 2. It consists of two dishes made from 60-mm. Pyrex standard wall tubing, flanged and ground so that a tight seal is formed when one dish is inverted on top of the other. Two glass hooks are mounted in the top dish approximately 7 mm. from center. The length of each hook is 15 mm. Suspended between each hook is a 1-ml. beaker provided with two 7-mm. glass arms attached on opposite sides of the rim of the beaker. This beaker holds the starch-potassium iodide indicator solution. A 5-ml. beaker is half filled with water and placed in the center of the bottom dish. The halogen-releasing disinfectant is placed in the bottom dish around the 5-ml. beaker and the specimen to be tested is mounted between the top and bottom dishes. A silicone lubricant is used to coat the ground rims of both dishes to assist in obtaining a reasonably tight seal against sample specimen.

During storage at 37 deg. C., four to five times the number of improved test cells can be accom-

Table I: Resistance of various packaging materials against chlorine and iodine vapors

(37 deg. C. and 100% relative humidity)

Material	Days' protection afforded against Chlorine vapors: As a sheet	Chlorine vapors: As a pouch	Iodine vapors: As a sheet	Iodine vapors: As a pouch
1 Control (25-lbs. polyethylene laminated to 3.5-mil aluminum foil to 5-lb. polyethylene to 25-lb. pouch paper with lacquer coating)	5	10	7	15
2 0.5-1.0-mil Mylar laminated to waxed* 40-lb. kraft paper	119	41	159	68
3 1.0-mil Mylar laminated to waxed 25-lb. white sulfite paper	10	62	151	10
4 0.5-mil Mylar laminated to 1.0-mil single-wound saran	31	21	133	21
5 1.0-mil single-wound saran	2	15	6	17
6 1.0-mil Mylar	2—180†	2	3	2

*Wax coatings used in all tests consisted of a mixture of microcrystalline wax and polyisobutylene as described in Specification MIL-T-283C.

†The average 1.0-mil Mylar gave only two days' protection against chlorine vapors. In one experiment, 180 days' protection was obtained, but this is considered the exception, since this particular sample of Mylar was probably void of fault counts.

Table II: Water-vapor transmission rates of various packaging materials

(23 deg. C./53% relative humidity)

Material	WVTR in gm./100 m.²/hr.
1 Control (25-lbs. polyethylene laminated to 3.5-mil aluminum foil to 25-lbs. polyethylene to 25-lb pouch paper with lacquer coating	0.0-0.5
2 0.5-1.0-mil Mylar laminated to waxed 40-lb. natural kraft paper	1.0
3 0.5-1.0-mil Mylar laminated to waxed white sulfite paper	1.0
4 0.5-mil Mylar laminated to 1.0-mil single-wound saran	2.3
5 1.0-mil single-wound saran	2.1
6 1.0-mil Mylar	26.0

modated in the equivalent amount of incubator space formerly required. Other advantages are smaller dimensions of the test specimen (9 by 9 cm. vs. a minimum of 20 by 20 cm. specimen size) and the comparatively small amounts of halogen-releasing disinfectant required when using the improved test cell instead of the standard laboratory desiccator test cell.

A number of tests have been run on some of the more common packaging materials. The results of these tests in terms of the number of days each material provided protection against chlorine and iodine vapors are shown in Table I. They represent an average of three tests and, in some instances, as many as eight. The control packaging material used in this study is the standard packaging for Disinfectant, Chlorine, Food Service, Specification MIL-D-11309A, previously described. Single sheets and pouches of the various packaging materials were evaluated. Heat-sealed pouches of the halogen-releasing disinfectant were tested by placing the pouch in the desiccator containing 100 ml. of water and a small beaker of a starch-potassium iodide indicator. This desiccator was assembled and the pouch exposed to approximately 100% relative humidity at 37 deg. C. until the indicator turned blue.

Results

In an early experiment, a sample of 1.0-mil Mylar film gave 180 days' protection against chlorine vapors, but all subsequent experiments with Mylar gave only two days' protection against chlorine vapors. The sample of Mylar film that gave 180 days' protection against chlorine vapors was undoubtedly a film with no fault counts, thus providing an ideal barrier against chlorine vapors. However, the average 1.0-mil Mylar film contains a degree of fault counts which are inherent in its production and which limit its chlorine-barrier characteristic to approximately two days.

A comparison of the results obtained with the various laminates evaluated shows that Mylar film laminated to waxed 40-lb. kraft gave the best protection against chlorine and iodine vapors. The Mylar film laminated to waxed 25-lb. white sulfite paper gave the next-best protection against chlorine and iodine vapors, while the Mylar laminated to saran was considered third in its ability to resist the vapors of chlorine and iodine. In noting the brief duration of the protection offered by Mylar, saran and wax-coated kraft alone, it can readily be seen that the phenomena operating in the various laminated materials represent not merely an additive effect of the protective qualities afforded by the individual constituents of the laminate. For example, it will be noted that a single sheet of 1.0-mil Mylar alone gives only two days' protection against chlorine vapors. The wax-coated kraft paper in sheet form gives 10 days' protection against chlorine vapors. If the phenomena operating here were simply an additive effect, the total number of days' protection against chlorine should be obtained by adding the number of days' protection afforded by Mylar alone plus the number of days' protection afforded by the wax-coated kraft paper alone. Thus, if this were true, the laminate of Mylar to wax-coated kraft should give only approximately 12 days' protection against chlorine vapors. However, in examining the results in Table I, 119 days' protection against chlorine vapors is obtained using the Mylar-wax-coated-kraft laminate. Such results definitely show the number of days' protection is not additive, since much greater protection is obtained against chlorine using the Mylar-wax-coated-kraft laminate than is obtained using either of the individual components.

In comparing the protective qualities of a single sheet with a pouch of the material under test, there is considerable variation in the results. These differences can probably be explained by the fact that all applications of the wax coating and the heat seals used on the pouches were performed under limited laboratory facilities, which were in several instances inadequate. For example, the deposition of the wax coating on the pouches tested varied between 0.5 and 4 mils. The pouches were hand dipped in molten wax after they were filled and sealed. This made it difficult to control the actual amount of the wax deposit on each pouch. Better control over the deposition of wax on single sheets was obtained through the use of hot-wire-wound coating rods so that the wax deposition varied between 1 and 2 mils. The greater variation in the amount of wax deposited on the pouches probably accounts for the erratic type of pouch protection vs. single-sheet protection as reported in Table I.

One additional observation may be noted in the use of saran and Mylar/saran laminates. In a matter of only a few days, iodine and chlorine releasing disinfectants appear to react or combine with the saran alone and with the saran when used as a laminate with Mylar. This is illustrated by the dark brown color imparted to saran when used in packaging iodine-releasing disinfectants and by the milky appearance imparted to saran when used in the packaging of chlorine releasing compounds. This might be considered an objection to using saran for packaging chlorine and iodine releasing disinfectant formulations.

Since the amount of halogen released from a packaged disinfectant is somewhat proportional to the amount of moisture gaining entrance to the package, water-vapor transmission rates were determined for some of the packaging materials used in this study. The water-vapor transmission rates (WVTR) were run according to ASTM Designation E 96-53T, Procedure B, Part 7, 1955, except that relative humidity was controlled at 53% instead of 50 ± 2%. Also, no attempt was made to control the circulation of air at 500 ft. per minute.

Table II lists the WVTR for some of the materials tested. The material which gave the best protection against water-vapor transmission was the control sample. When a laminate of polyethylene-aluminum foil paper is evaluated against chlorine and iodine vapors, the foil is readily attacked by the halogen and severe pitting of the foil results. Consequently, the good moisture-barrier characteristics of such a laminate are gradually lost as the foil is eaten away.

The Mylar laminate to 40-lb. kraft and the Mylar laminate to white sulfite paper give the same WVTR values. However, the natural kraft appears to give better protection against the vapors of both chlorine and iodine. The saran/Mylar laminate and the saran film alone show about the same WVTR. The difference between 2.3 and 2.1 WVTR for the Mylar/saran laminates and saran, respectively, is not considered significant. However, the Mylar/saran laminate gives far superior protection against the vapors of chlorine and iodine than saran alone. One-mil Mylar alone showed the poorest protection against water-vapor penetration as well as chlorine and iodine vapors. The agreement between the samples showing the lowest WVTR and the longest protection afforded against iodine and chlorine vapors, although not perfect, is fairly good.

Since the 0.5- to 1.0-mil Mylar laminated to waxed 40-lb. kraft gave the best protection among the waxed laminates tested and the saran/Mylar laminate also showed considerable promise as a potential packaging material, a small commercial production run using these packaging materials and Disinfectant, Chlorine, Food Service, will be undertaken. This will establish whether or not pouches of these laminates can be feasibly produced on commercial production lines. If pouches can be produced commercially, a storage-stability study is contemplated to obtain the degree of protection such pouches will afford under various climatic conditions.

Acknowledgement

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