On the Cold Storage of Photographic Materials in a Conventional Freezer Using the Critical Moisture Indicator (CMI) Packaging Method

Mark H. McCormick-Goodhart

Preface

The paper you are about to read is actually a draft that was never completed for publication. I wrote it in 1994 while I was a research scientist employed by the Smithsonian Institution in Washington DC. I was interested in low cost methods of cold storage that could be used for small collections of photographic films and prints. Many photographers seek a better way to preserve their life's work, and small historical societies can also benefit from the principles of the CMI packaging method. Even large institutions don't always have the resources to undertake expensive vault building projects to the extent that they are needed, and a small scale approach is far better than doing nothing. Yet I didn't publish the paper because I felt it lacked information on the subject of "staging" (i.e., transfering the package to and from the freezer). At the time the primary concern for conservators appeared to be twofold: 1) How long does it take to warm them before opening the package, and 2) Will the photographs be damaged by thermal cycling? In more recent years, new cold storage research that I have been conducting with my good friend and colleague, Henry Wilhelm, has uncovered the potential for a third problem. We have seen that large, loosely filled containers, even though they may have an outer vapor barrier, can have internal moisture migration problems during the warm-up and cool-down stages. Thermal gradients, moisture gradients, and warming times are thus interelated. Elimination of the risks for all shapes and sizes of packages requires some basic understanding that is beyond the scope of this paper. However, a brief explanation that will enable safe adoption of the CMI packaging method is as follows:

Thermal shock was answered to my satisfaction by my Smithsonian colleagues and myself with research we conducted in the early to mid 1990s. *The thermal gradient existing during warm-up or cool-down periods is not enough to cause the prints or films to reach unsafe levels of thermal stress.* However, warming time and cooling times vary by size, insulation, and mass of the package. A large thermal gradient does not cause damage directly. Rather, it indirectly can lead to a moisture gradient inside the package whereby hygroscopic materials located near the outside walls of the package can warm faster and consequently release moisture which then raises the relative humidity in the cooler interior parts of the package. The warm-to-cool gradient reverses when the package is to be cooler rather than warmed. In extreme cases, condensation inside the package may occur. A vapor barrier covering the outside package eliminates the external source of moisture, but cannot eliminate the internal moisture migration which may occur when the thermal gradient across the package contents is too large. The solution is to make sure the thermal gradient is not too large, and it can be achieved three ways:

1) Use a temperature staging chamber (an expensive but valid approach).

2) Add temperary insulation and mass to the package (e.g. place the package in a "picnic cooler" box possibly containing additional thermal mass).

3) Keep the package mass low and thickness realatively thin so that a large thermal gradient cannot occur.

In all three cases, the simplest way to determine when the package has warmed so that it may be safely opened is to monitor or predetermine its temperature response. From the preceding discussion, it is clear that no single answer can be provided to work for all objects of all sizes, but the CMI method lends itself to a modular design with predictable warming behavior. Thus, I can confidently say that CMI packages 1.5 inches or less in thickness containing film or print materials and with low free space in the inner bag are safely "self-staging". The statement in this paper's "Introduction" referring to scalability of the CMI design therefore requires minor clarification. The CMI package design can be scaled by length and width but should not exceed 1.5 inches in thickness unless additional steps are taken to thermally insulate the package during transition to and from the freezer. For small collections to be placed in domestic reach-in freezers (i.e., household appliances), the 1.5 inch thick package is an appropriate modular unit that is easy to handle. A commercial CMI package design adhering to this specification is currently available for sale by Metal Edge, Inc., 6340 Bandini Blvd., Commerce, CA 90040 (metaledge.com, 1-800-862-2228). The product is called the "Image Archive Freezer Kit". The kit makes five packages. *Each package is 1.5 inches thick and safely warms to room temperature in about three hours without any additional handling considerations.* Because the original research for the CMI design was funded by the Smithsonian Institution and by a grant from the Imperial Archives Limited partnership, Burbank, CA, the CMI method is entirely in the public domain. I have no vested commercial interest in the product or royalties derived from it, and I would welcome other conservation supply companies to bring products based on the CMI concept to the market.

This current version of the paper has been reformatted as a PDF file and remains unchanged in content though slightly different in layout compared to the original paper. Some of the information listed in the appendix is more than likely out of date at this point in time. Additionally, I added figure 10 to the draft in about the year 1996. Figure 10 shows the drop-front conservation box style that was to become the basis of the Image Archive Freezer kit. As the original draft was authored over ten years ago, I have had to "migrate" the text from an early WordPerfect format to Microsoft Word format and more recently to Adobe Indesign. The photos and figures were more problematic. The original figures were made with "Freelance Graphics" software and slide scans in tiff format that were unfortunately not embedded. Most of the images in figures 2,3, and 10 did not survive in electronic form. Reconstruction of these pages from the original slides was just too time-consuming so I simply rescanned these pages from hardcopy inkjet prints that I did have in my records. The image quality has suffered but the concepts are still illustrated satisfactorily. All the figures are located at the back of the document in landscape format as they were in the original draft, and it is therfore easier to read a printed copy rather than to try to read on a computer monitor.

In the section on CMI indicators located on page 9, I referred to the cobaltous chloride indicator cards as relatively non toxic. Toxicity data on cobaltous chloride seems to vary widely and is dependent on the form in which it is handled. When applied in small quantities to blotter paper, the final product presently meets all federal and local codes in the U.S. as a non hazardous material. When added to silica gel, concerns increase due to the larger volumes of material that are handled and the tendency for silica gel to produce airborne dust particles that are more easily inhaled. I have appended to the end of this document a "*Conserv O Gram*" published by the National Park Service that addresses this issue.

On a final note, I started my own personal freezer collection in 1991, and that effort led to the development of the CMI method. Some of my earliest CMI packages are almost ten years old now. The collection is not accessed frequently, but it is carefully and routinely monitored. I have not yet had a package indicator turn lavender or pink, nor have I observed any further chemical or physical deterioration to any of the images I have retrieved from the freezer. They remain as they appeared to me the day they went into storage. In addition to my own collection, numerous examples of the CMI cold storage approach can now be found in practice at museums, archives, and in the private sector. The CMI method of cold storage works!

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July 31, 2003

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Introduction:

High-moisture-barrier packaging materials of the kind used in the FICA system have very low permeability to moisture vapor.[1] High-moisture-barrier packaging assumes that each package has a "perfect" seal and that no other defects exist in the package walls. The only non-invasive way to monitor the performance of these packages over time is by weighing each package. To the author's knowledge, weighing techniques are seldom used, so high-moisture-barrier bag procedures essentially rely on excellent package quality. In contrast, the critical moisture indicator (CMI) package described in this paper is assumed to be an imperfect moisture vapor barrier which allows moisture to diffuse through the bag wall, seals, and small pinholes over time. The CMI method works because water vapor diffusion rates at freezer storage temperature (0ºF/-18ºC) are dramatically reduced and also because reserve moisture buffering capacity is enclosed inside the package.

The physical features of the CMI design are shown in figure 1. This generic package design is both predictable and verifiable. It can also be scaled to different sizes without affecting its performance. The CMI method is explained in detail in this paper so that its safety and function will be well understood, but this attention to detail may give the impression that the package is elaborate and difficult to use. In practice, the method is actually very simple, but the only way to find out is to try it! Two optically clear, low density polyethylene (LDPE) bags are used, an inner bag nesting inside the outer bag. The photographic materials are placed inside the inner bag. A *moisture trap* and a *critical moisture indicator* (CMI) are placed between the inner and outer bag. The moisture trap is comprised of a low volume of hygroscopic material which is dried before use, e.g., 4-ply conservation mat board or silica gel. The photographic materials are isolated from the desiccated trap materials and doubly isolated from the freezer environment. The CMI is made of blotter paper imbibed with cobaltous chloride. Cobaltous chloride is widely used as a relative humidity indicator and tailored to indicate a particular relative humidity value at a specified temperature. In point of fact, the cobaltous chloride responds directly to the moisture content of the blotter paper and only indirectly to water vapor in the air, so it closely mimics the hygroscopic behavior of photographic materials over a wide temperature range. The CMI turns color from blue to lavender as its moisture content reaches a specified critical value. As the critical moisture value is exceeded the indicator continues to turn color from lavender to pink. By observing the color of the CMI, the safety of the package can be verified at any time, and ample time is available to rescue failing packages because the moisture diffusion process is very slow in the freezer environment. To summarize, the complete CMI package is a microclimate within a microclimate. The microclimate created by the photographic materials in the inner bag is surrounded by the protective and sacrificial microclimate established by the moisture trap, and the critical moisture indicator is a visual safety monitor that can be observed at any time through the clear LDPE bag.

Moisture Content of the Trap versus Moisture Content of the Photographic Materials:

Recommendations to moisture condition photographic materials by prolonged exposure to low relative humidity levels (e.g., 25-30% RH) at room temperature prior to cold storage are found in the photographic conservation literature.[1,2,3] Unfortunately, moisture conditioning photographic materials can be time consuming, and the time varies according to the type and volume of material to be stored and the temperature of the environment. In the CMI packaging procedure, precise control of the moisture content in the photographic materials is not a prerequisite for safe packaging. The photographic materials are allowed to be in equilibrium with any moderate relative humidity level (i.e., 35 to 60% RH) at room temperature. This equilibrium state is easily met by making sure that the collection materials are not exposed to high or low humidity conditions for long periods of time, a recommendation that makes sense even for room temperature storage and use. No further conditioning is required or recommended. The materials can be inserted directly into the inner bag. Only the moisture trap materials are subjected to moisture conditioning. Because they are not collection objects, these materials are expendable and can be consistently and repeatedly heat-dried in a short amount of time. The moisture conditioning procedure can be done immediately prior to sealing the package, or a supply of preconditioned moisture trap materials can be prepared in advance and used as required. There need be no delay in returning photographic materials from use to storage, an important consideration when managing a cold storage vault.

Directions for Packaging Photographic Materials in the CMI bag:

The following directions describe a CMI package using LDPE bags with reclosable ("zip lock") seals and made to fit letter-file size folders. Letter-file folders routinely accommodate photographic films or prints in a wide variety of formats. Other size packages can be made by following the generic design features illustrated in figure 1. Figure 2 shows photos of this style of package and illustrates the packaging sequence which is now described:

<u>Package Components:</u>

1. LDPE inner bag.
2. LDPE outer bag.
3. Two 4-ply (.060 inch thick) mat boards.
4. Cobaltous Chloride (CoCl) humidity indicator (specify to turn lavender at 25 deg. C, 60% RH).
5. Cover jacket, 0.010 to 0.020 inch thick card stock.

Note: A cover jacket is not shown in figure 1. It is optional but convenient for recording catalog #'s, package #s, or bar codes and for attaching the CMI indicator to an easy viewing location. The jacket is located between the inner and outer bag, and arranged to suit personal preference.

1. Carefully insert the file folders containing the sleeved photographic materials into the inner bag, and close the seal.

2. Insert the inner bag into the outer bag.

3. Slide the cover jacket with affixed CMI indicator into the outer bag, arranging it to cover the inner bag and display the CMI indicator so that it is in full view.

4. Insert two pre-dried 4-ply mat boards, one on each side of the inner bag as shown in figure 1.

5. Double check that the inner bag is sealed, and then close the seal on the outer bag. The package is ready for storage in the freezer.

Note: The order of the preceding steps can be varied to suit individual handling preferences (e.g., steps 2, 3, and 4 can be rearranged).

As an example, approximately two hundred 35mm slides located in ten letter-file size plastic slide pages will fit neatly into a reclosable CMI package about 1 inch thick. This reclosable CMI package can be prepared in about one minute. By assembling individual packages no greater than one inch thick, more convenient access time is gained. The warm-up time for this style of package is approximately two hours. When using LDPE bags, care should be taken not to trap additional air inside the bag. Otherwise, it will tend to form a "pillow" with unwanted extra thickness, and the possibility of reopening exists when compressed against other packages on the shelf. The user will evolve personalized techniques to achieve a form fitting package. In the event of a breached seal in storage, the moisture trap still functions for several months whereupon the CMI indicator slowly turns from blue to lavender and eventually to pink. Packages do not fail quickly at sub-zero temperature because moisture vapor diffusion rates are very slow, even through slits, cracks, or holes in the LDPE. An important safety feature of the CMI design is that failing packages can be easily caught in time by routine visual inspection.

Preparing the Moisture Trap.

Preparing the moisture trap is probably the most difficult part of the CMI method, but it is not very labor intensive and is more practical than conditioning the actual photographic collection materials. There are a variety of materials that can be used to make a moisture trap. Two useful ones are mat board and silica gel. Silica gel is supplied pre-dried by the manufacturer and is re-activated by heat drying in an oven according to the manufacturer's instructions. Silica gel works well when the CMI method is adapted for use with motion-picture film as shown in figure 3. For the "letter file" CMI package shown in figure 2, two sheets of 4-ply mat board are used to create a moisture trap. Mat board is easily and quickly dried in a conventional oven.

1. Place the mat board in a standard convection oven for 3-5 minutes at 100ºC.

2. Make sure that the full surface area of each board is exposed in the oven in order to maximize the drying process and minimize curling which can occur if moisture is not allowed to leave all surfaces of the board. Multiple oven racks are useful to dry more boards at one time.

3. Allow the boards to cool before insertion into the CMI package.

The boards may continue to lose some moisture just as they are removed from the oven so it is helpful to keep their surface area exposed briefly during the initial cooling period. After returning to room temperature, the boards can be handled for several more minutes before they reabsorb significant moisture. Boards may be prepared in advance and kept ready for use in an appropriate moisture tight container for many days or weeks. A CoCl humidity indicator card (specify 10%, 20%, or scale indicator for this monitoring application) can optionally be used to show that the boards have retained their pre-dried moisture content quality. Interchange ability of parts is desirable in the CMI method. Standardizing on the size of the package and mat board and writing package I.D. information elsewhere than on the mat board allows any board to be inserted into any one of the packages as they are prepared once again for cold storage.

Temperatures as low as 70º C will effectively dry the mat board to a moisture content level of approximately 1 percent, but drying time varies with temperature. Figure 4 documents the 4-ply mat board drying process. A 1% moisture content value is reached in about 3 minutes at 100ºC. The lower the initial moisture content of the mat board the longer the shelf life of the package. Thoroughly dried board will establish a 19 year shelf life in the freezer (-18ºC), but good shelf life can be obtained with less rigorous drying. Table I lists the shelf life performance of the packages when the mat board has been tried to various levels of dryness. Figure 5 plots the rise in moisture content in the mat board over time , i.e., the consumption of the package shelf life. The shelf life is fully consumed when the critical moisture content value is met. A 6.0 percent moisture content value has been set for the critical value in the 4-ply mat board because it establishes an equilibrium RH within the bag of 60% RH when the CMI package returns to a warm room temperature (25ºC). This environmental condition is the maximum allowable RH and temperature in which photographic materials are chemically and physically safe and mold growth or emulsion sticking will not occur. The cobaltous chloride indicator is therefore also specified to turn color at 25ºC/60% RH. When an indicator turns lavender it is time to re-activate the moisture trap by replacing the mat boards with freshly dried boards.

Risk of Desiccating the Photographic Materials:

The risk of accidentally desiccating the photographic material is low with the CMI method because only a small volume of moisture trap materials are used and also because the inner bag is isolated from the moisture trap. Over the long shelf life of the CMI package, the photographic materials will initially lose small amounts of water by diffusion through the inner bag wall, but water is simultaneously diffusing inward through the outer bag so that the average long term relative humidity in the moisture trap seeks a moderate value. In the event of an inner bag failure, e.g., forgetting to close the seal, the photographic materials exchange moisture with the moisture trap more rapidly. Normally, the moisture buffering capacity of the photographic material and paper enclosures in the inner bag is enough so that the total group of materials would not attain a severely desiccated state due to the presence of the dried mat board. However, one caveat is worth noting. If a very small amount of photographic materials was located in the inner bag such as a single plastic page of 35mm slides without a paper file folder, the very dry mat board could establish too low an RH level with the improperly functioning inner bag.

There are numerous ways to circumvent this potential problem. Filling the inner bag completely with photographic and paper products is a good way to guarantee that this situation will not occur. If there are not enough photographic materials to fill an inner bag, "bulk up" the moisture capacity of the photographic contents by adding two or more additional mat boards to the package *that have not been pre-dried.* The moisture trap materials, additional non-dried mat boards and the photographic materials will then equilibrate to a safe new relative humidity level in the event that the inner bag is not functioning normally. Package shelf life is either unaffected by this action or actually increases. When the photographic materials and any additional items which are inserted into the CMI package are precisely at 60% RH equilibrium at room temperature they neither add to nor subtract from the performance of the moisture trap. When they are in equilibrium with lower RH levels at room temperature, they will only *add* to the moisture buffering capacity of the package. Shelf life of the package will be extended. Hence, the prediction of shelf life for the CMI package is nearly always underestimated by considering just the material properties of the moisture trap material alone. The moisture trap always guarantees a minimum shelf life for each properly functioning package, and the critical moisture indicator identifies the few that are not performing up to standard and when it is time to recondition the moisture trap.

Package Shelf life:

From a technical standpoint, the merit of this package design rests on its ability to provide an adequate moisture trap without requiring a large volume of material and also its ability to free the user from having to make repeated calculations or have precise knowledge about weight, material type, or equilibrium moisture state of the photo materials. One advantage of the 4-ply mat board is that it creates a generic package style. This generic package can be scaled to any size by cutting mat board to just fit the size of the LDPE outer bag. As the package increases in size the surface area of the package also increases which in turn increases the total amount of water that can enter the package per unit time. However, the mat board volume also increases proportionately as the package is scaled larger, and so its moisture absorbing capacity increases as well.

Shelf life can be calculated by an equation that was originally derived by food packaging scientists.[4] The equation is presented in order to defend the predictable nature of this packaging method, and to explain how one would calculate the amount of silica gel or other desiccant material that could be used to make the moisture trap. It is a very useful equation for engineering a desired shelf life into a specific package design or, for example, estimating the moisture buffering performance of framing materials in an exhibition environment. However, understanding how to use the equation is not essential to the successful implementation of the CMI method. The reader may choose to skip this section.

The shelf life equation is:

$$t = \frac{m_D \Delta a'}{100 P_w}[\frac{X_k - X_0}{a_{wk} - a_{w0}}]2.303\log[\frac{a_{wa} - a_{w0}}{a_{wa} - a_{wk}}]$$

where t = shelf life (i.e., the length of time that the trap will provide satisfactory moisture control during storage),

m_D = dry weight (grams) of packaged product (e.g., the moisture trap material)

X_0 = initial moisture content of packaged product

X_k = critical moisture content of packaged product

a_{w0} = initial water activity

a_{wk} = critical water activity

a_{wa} = water activity of environment surrounding the package

P_w = Water vapor permeability of the package (e.g., grams per unit area per day multiplied by the surface area of the package)

a' = water activity difference during test conditions to determine P_w

Moisture content and water activity data needed to solve the shelf life equation can be estimated from moisture absorption isotherm data. This data is provided for typical conservation quality mat board and for silica gel in figures 6 and 7. The term "water activity" is equal to relative humidity (RH) divided by 100. The moisture vapor transmission rate (MVTR) for 4 mil thick LDPE was measured in our laboratory to be 0.008 grams per square meter of surface area per day at -18^{o}C (O^{o}F) where a' = 0.63 (typical conditions met by a conventional freezer). P_w, the water vapor permeability of the package, is calculated by multiplying MVTR times the total surface area of the package. Remember to include both sides of a bag and to keep the units of measurement consistent when determining P_w. At room temperature (22^{o}C) the MVTR of 4 mil thick LDPE rises to 1.2 grams per square meter of surface area per day, an increase of two orders of magnitude! Shelf life of the package drops dramatically as shown in the test data compiled in figure 8. The data in figure 8 show that the equation accurately predicts package performance. Collectively, figures 5 and 8 demonstrate that 4 mil LDPE bags give excellent long term moisture protection at freezer storage temperature, and also very good short term protection at room temperature in the event of total freezer mechanical failure going uncorrected for several days. The following data represents the properties of the CMI letter-file package stored at -18°C:

m_D = 126 grams

P_w = .00165 grams/day

a' = .63

X_0 = 1.0%

X_k = 6.0%

a_{w0} = .05

a_{wk} = .43

a_{wa} = .65

Recall that the term water activity is equal to RH divided by 100. Also, the value a_{wk} = .43 reflects the fact that the desired endpoint of 60% RH at room temperature is equal to approximately 43% RH at -18ºC as shown in the moisture isotherm data of figure 6. This RH shift inside the package as temperature is reduced is a natural consequence of the hygroscopic properties of the film materials sealed in a vapor proof package with little free air space (3). The freezer RH was taken at 65% RH (a_{wa} = .65), the highest value of several different types of freezers that were measured. X_0 and X_k are also determined from the standard absorption isotherm data for the mat board (see also, figure 5).

Materials and Supplies:

Unless the CMI method becomes more widely used, the supplies needed to make a CMI package will not be entirely available from the customary conservation materials and supplies catalogs. At the present time the end user must order items from separate vendors, and perhaps customize the LDPE bags to suit individual applications by hand. The vendors listed in Appendix I by no means constitute a comprehensive list but have been used by the author during the course of research on the CMI project.

<u>Low Density Polyethylene bags:</u>

LDPE bags of the plain or reclosable variety can be obtained at a variety plastic packaging vendors. These vendors routinely make custom sizes, but unfortunately, the minimum order is likely to be over 10,000 bags. However, a wide range of stock sizes are available. With care and a little effort, an inner bag of the same size as the outer bag can be enclosed. Nonetheless, the author prefers to hand craft a smaller inner bag by fabricating it from a stock size bag that has been purchased to function as the outer bag. For example, the letter file size CMI package shown in figure 2 had a 12.5 inch reclosable width by 11.0 inch deep (bottom edge to seal) inner bag. The outer bag was 13 inches wide on the reclosable edge and 12.5 inches deep (bottom edge to seal). Both bags were handcrafted from stock 4 mil thick 13 x 18 inch LDPE bags, a standard industrial size. To modify stock bag sizes by hand, a variety of heat sealing and cutting devices are available from plastic bag vendors. Some work much better than others, but most are relatively inexpensive, usually $100-$200.

There have been some quality related issues with the LDPE bags. The reclosable seal on one popular brand of reclosable bag undergoes an additional heat pressing step which further "pinches" the bag at the edges. The vendor claims that the bag is easier to close, but this extra finishing operation also tends to put pinholes in the bag right below the seal at the edge of the bag. On a practical note, the pinched edges also slightly restrict the effective opening width of the seal making it harder at time to insert form fitting materials into the bag. Coincidentally, this brand of bag was used to generate the MVTR data reported in this paper so the shelf life calculations have already taken into account the reduced quality of this type of bag and reclosable seal. Additionally, it should be understood that reclosable LDPE bags are highly water resistant but not guaranteed leak proof by the vendors. The most common place they leak is, perhaps surprisingly, not along the seal itself or the edges of the bag in general, but directly through the edge of the seal. This is because the extra plastic associated with the reclosable seal is harder to completely melt as the bag is trimmed to size by the manufacturer using a "hot wire" technique. Nonetheless, tests conducted by the author on the CMI package show that the photographic materials are greatly protected from water damage, especially compared to the nonexistent level of protection afforded by ordinary archival document boxes. The CMI package will withstand a "rain shower" and also full immersion under water for several minutes, but longer periods of full immersion will ultimately affect the photographic materials in the inner bag. In the event of a disaster in the archive involving water or flood damage, the CMI's color change should help to alert staff to the water damaged bags in the collection. The failing packages can be given priority status during disaster recovery operations.

A recently developed LDPE bag has just come on the market and it is guaranteed to be leak proof. It has a unique reclosable seal and is reinforced with a wider heat seal all around the edges. This type of bag is presently being investigated for use with the CMI method by the author.

<u>Mat Board:</u>

Conservation quality mat board in 4-ply thickness is readily available from the conservation supply catalogs. For the letter file size bag, an appropriate board size can be cut to 9.5 x 11.75 inches, the standard dimensions of the letter file folders. It is recommended that the corners be rounded (1/4" diameter) to reduce the risk of puncturing the LDPE when the boards are inserted.

Silica Gel:

Silica gel is available in a number of different grades. Figure 6 data shows a typical grade that meets MIL-D-436-4E. This specification requires that one unit (approximately one ounce of silica gel) absorb at least 3 grams of water at 20% RH and at least 6 grams at 40% RH at 25ºC. Other types can be used, but the moisture isotherm data may differ significantly.

CMI indicators:

The CMI indicator is made to the author's specification by Humidial Corporation. Humidial Corporation will make small quantities of single value humidity indicators with a vinyl adhesive backing. The backing is optional, but a 0.5 by 0.5 inch square (specify 60% RH@25ºC) with adhesive backing is very convenient for this application. Cobaltous chloride indicator cards are relatively non-toxic, but colbaltous chloride is a metal salt and should not be placed in direct contact with photographic materials. Located in between the two bags and with such a small size, the cobaltous chloride and the vinyl adhesive backing pose insignificant risk to the collection materials.

Freezers:

The CMI package will work properly in any conventional freezer. Conventional freezer technology is offered by a large and mature industry. Both manual and autodefrost reach-in freezers can be purchased in capacities ranging from 10 cu. ft. to 70 cu. ft. Modular cabinet designs used by supermarkets in frozen food isles can be combined to form long banks of reach-in freezers. Capacities greater than 2000 cubic feet are possible with this type of technology. Reach-in freezers make good sense for small collections, and ones with fully adjustable shelves are recommended. For larger collections, walk-in freezer technology is much more economical. Walk-in freezers are scalable from small room-sized vaults all the way to giant warehouse facilities. Walk-in freezers use panel walls similar if not identical in construction to custom dehumidified vaults, but without the dehumifier equipment and electronic controls, their installation cost is significantly lower. As discussed in the following section, conventional walk-in freezers operate far more economically compared to 5ºC dehumidified cold vaults despite their sub-zero temperature. Autodefrost freezers complete a defrost cycle by turning off the compressor(s) and warming the condenser coil(s) to melt away the frozen water which leaves by a condensate drain tube. This step lasts about 25 to 40 minutes and is done once or twice each day. During this time the freezer compartment may warm several degrees, but the product temperature rises only one or two degrees due to the thermal mass. This daily cycle will not harm the photographic materials, nor does the cycle caused by taking photographic materials in and out of the vault. The CMI package completely insulates the photographic materials from the wide humidity fluctuations which occur operationally and when the freezer door is opened. Although the cycles can be of large magnitude, the average humidity is, perhaps surprisingly, similar for both manual and autodefrost freezers. Values between 50 and 65% RH are typical. The CMI package shelf life reported in this paper was determined for packages located in 65% average relative humidity freezers, the most severe situation.

Flammable material storage freezers and explosion-proof freezers are also available. Flammable materials storage freezers have spark proof interiors whereas explosion-proof freezers are spark proof on the interior and exterior. Unless the room where the freezer is located is also explosion-proof (designed with explosion proof outlets, lights, switches, etc.) there is no advantage to the explosion-proof freezer compared to a flammable materials storage freezer. Both types are a suitable choice for storing nitrate film.

Economics of the CMI Method Versus Custom Dehumidified vaults:

The CMI method was originally developed with smaller collections in mind. Conventional freezers are widely available in smaller sizes, and far less costly than custom dehumidified walk-in cold vaults. It seemed intuitively obvious that the additional labor and material costs associated with special packaging would eventually over time outstrip the original construction cost premiums for a custom vault. Yet collection management techniques needed to use the CMI method effectively with large collections can easily be implemented. These management techniques are more common in industry where inventory rotation practices are commonplace. Such practices required when photographic collections are stored in dehumidified cold vaults. However, when all of the differences are taken into account, and reasonable assumptions are made about frequency of access, operating, construction, labor, and material costs, the economics of the CMI method can be shown to be superior to traditional dehumidified cold vaults up to 9000 cubic feet total volume (30'w x 30'l x 10'h). A 9000 cubic foot walk-in freezer fitted with compact shelving could, for example, hold over 50,000 letter-file size CMI packages. This capacity would be able to accommodate over 10 million 35mm slides or more than 30,000 rolls of motion-picture film (1000 ft roll length)!

A rotational schedule to recondition 50,000 packages in accordance with their normal shelf life appears to be a daunting task. However, calculation will show that the task involves replacing the mat board on approximately ten packages per day which would take less than 20 minutes. This level of effort is clearly manageable. Larger vaults have not been evaluated by the author to date, but the CMI method is very competitive with the custom cold vaults most commonly built by museums and archives. The underlying reason is energy costs. Energy costs are estimated in figure 9. The extra labor, packaging, and inspection costs required with the CMI approach are more than offset by construction and energy savings when both approaches to cold storage are critically compared.

Final Remarks:

The CMI method provides an alternate approach to the cold storage of photographic materials. Considerable attention has been given during its development in order to ensure the safety of the photographic materials. However, there will always be risks associated with any cold storage method and this one is no exception. Users of the CMI method must accept full responsibility for the care of their collection materials. Neither the author nor the Smithsonian Institution can accept any liability for problems or damage that might be attributed directly or indirectly to the CMI packaging method. The risks associated with cold storage must always be weighed carefully against the risks encountered in room temperature storage of photographic materials. It is the author's deep conviction that cold storage, when implemented with care and forethought, is the most important thing that collection managers can do to extend the life of their collection. Individuals who try the CMI approach are respectfully encouraged to share their experience with the author.

Acknowledgments:

This research was made possible by a grant from Imperial Archives limited Partnership, Burbank, Ca. Many material samples were donated by University Products, International Plastics, The Bag Co., Humidial Corp. and United Desiccants, Inc. The author is deeply grateful for their patience and support.

References:

1. R. Goos and H. Bloman, "An Inexpensive Method for the Preservation and Long-term Storage of Color Film", J. SMPTE, **92**, 1314-1316, 1983.

2. P. Z. Adelstein, C. L. Graham, and L. E. West, "Preservation of Motion-Picture Color Films Having Permanent Value", J. SMPTE, **79**(11), 1011-1018, 1970.

3 G. T. Eaton, **The Conservation of Photographs**, Publication No. F-40, Eastman Kodak Co., Rochester NY, 1985.

4. K. Eichner, "The Influence of Water Content and Water Activity on Chemical Changes in Foods of Low Moisture Content under Packaging Aspects", chapter 5, **Food Packaging and Preservation Theory and Practice**, M. Mathlouthi, Ed., Elsevier Applied Science Publishers.

Table I: Shelf life of Package Created by Mat Boards at Varying Initial Moisture Content levels.

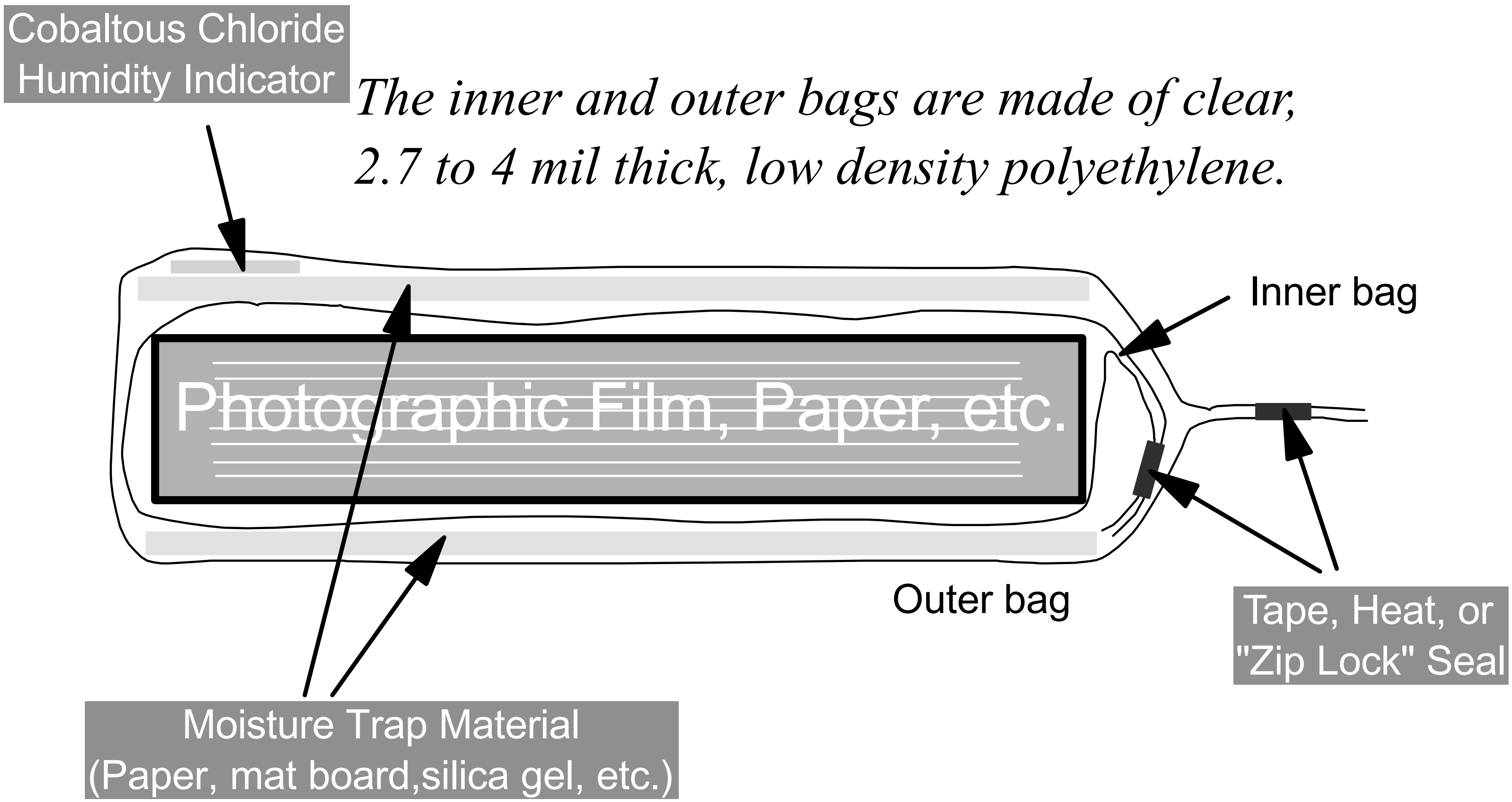
Initial Moisture Content	Shelf Life of Package
0	19 years
1	17 years
2	15 years
3	12 years
4	9 years
5	5 years
6	0 years

Appendix I:

Humidial Corporation: 465 North Mt. Vernon Ave. P.O. Box 610 Colton, CA 9234-0610 (909) 825-1793	Cobaltous Chloride Humidity Indicators
Light Impressions: 439 Monroe Ave P.O. Box 940 Rochester, NY 14603-0940 1-800-828-6216	Conservation Mat board
University Products, Inc. 517 Main Street P.O. Box 101 Holyoke, MA 01041-0101	Conservation Mat board
International Plastics 185 Commerce Center Greenville, SC 29615-9527 1-800-433-4043	LDPE bags
The Bag Co. 2145 Barrett Park Drive Suite 102 Kennesaw, Georgia 30144-3680 (404) 422-4187 1-800-533-1931	LDPE bags
United Desiccants 101 Christine Drive Belen, NM 87002 (505) 864-6691	Silica Gel
Hussman Corp. 12999 St. Charles Rock Rd. Bridgeton, MO 63044 (314) 291-2000	Walk-in freezers Modular System Reach-in Freezers Merchandizing Freezers
Kelvinator Scientific 707 Robins St. P.O. Box 4000	Laboratory Grade Reach-in Freezers Walk-in Freezers Flammable Material Storage Freezers

Safe &Verifiable Package Design for Freezer Storage of Photo Materials

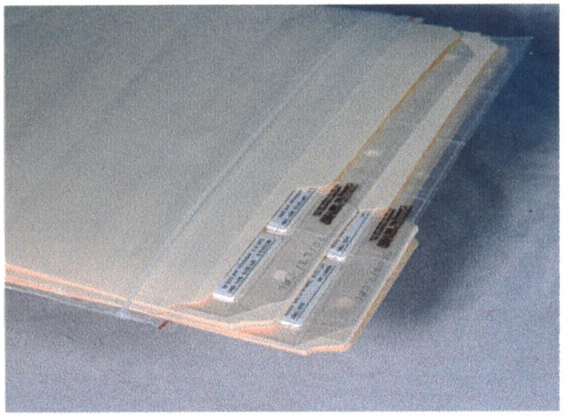
The inner and outer bags are made of clear, 2.7 to 4 mil thick, low density polyethylene.



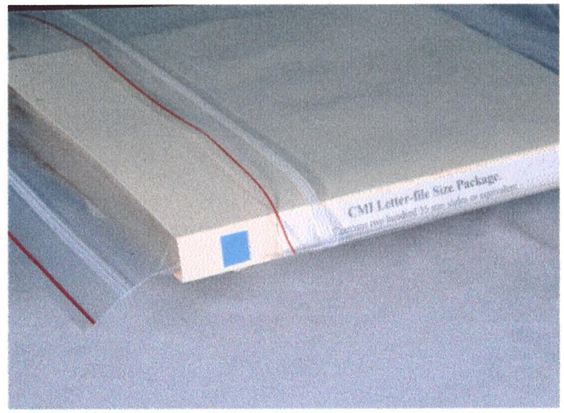
Smithsonian Institution
Washington, D.C.

Figure 1.

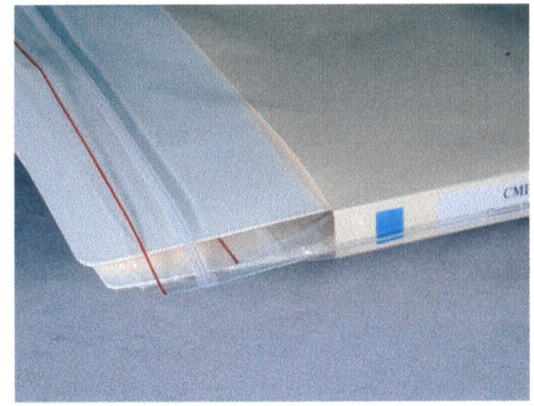
Letter-file Size CMI Package



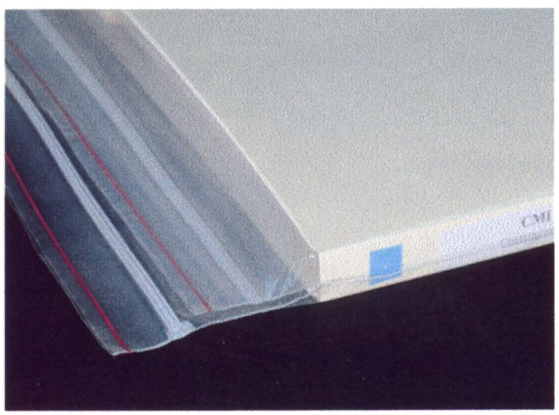
Step 1. Slide pages and file folders are placed in inner LDPE bag and bag is sealed.



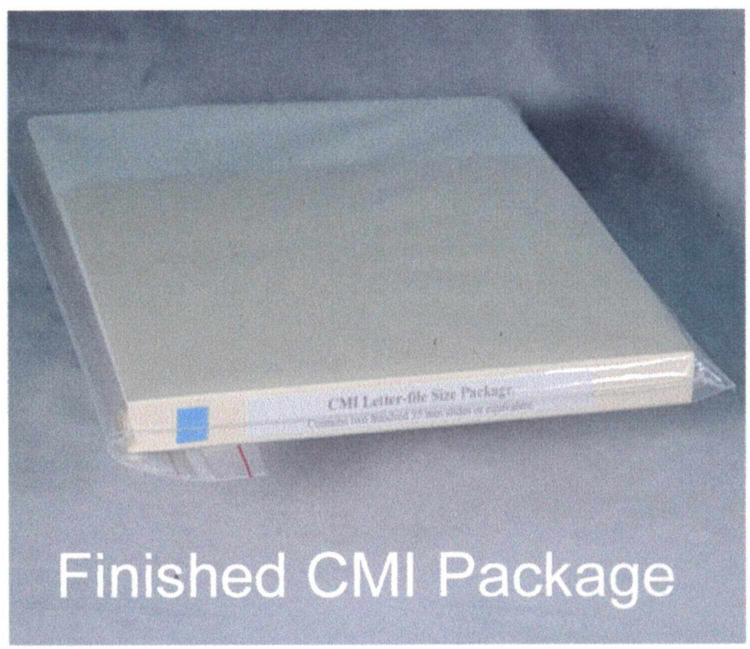
Steps 2 and 3. Sealed Inner bag and cover jacket with affixed cobaltous chloride indicator are placed in outer bag.

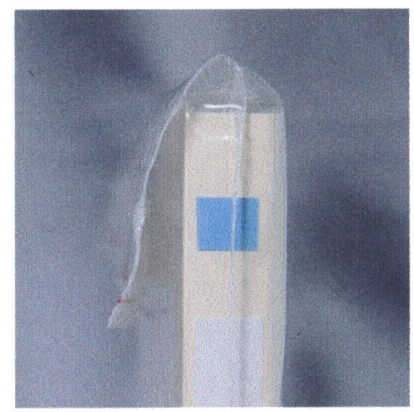


Step 4. Pre-dried 4-ply mat boards are inserted, one above and one below the inner bag.



Step 5. Seal on Inner bag is rechecked to make sure it is closed, then outer bag is sealed.



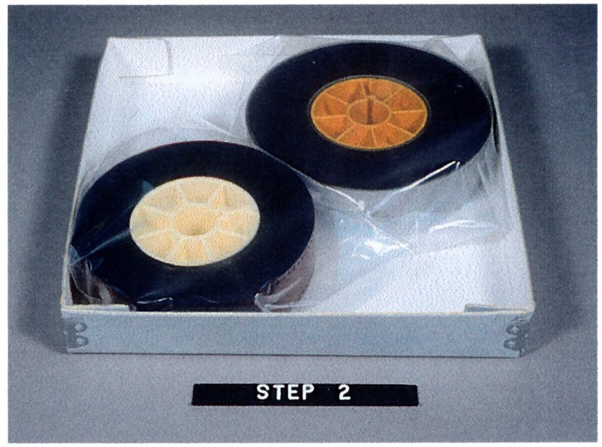


LDPE bags fold over and the package is vertically stored. The letter-file folders remain upright, and a "shingle roof" effect gives extra insurance against water penetration.

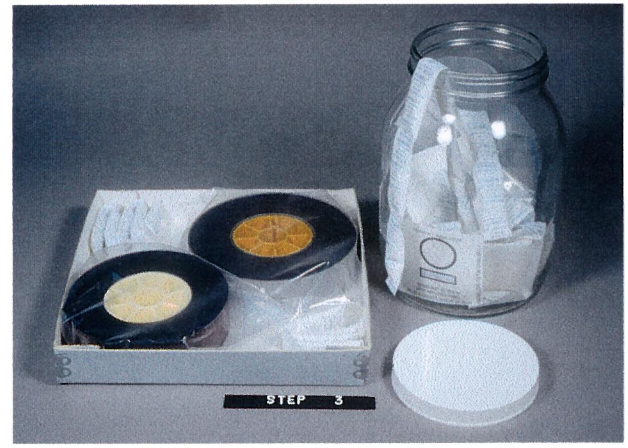
Figure 2.

CMI Package Design Adapted for Use with Motion-picture Film...

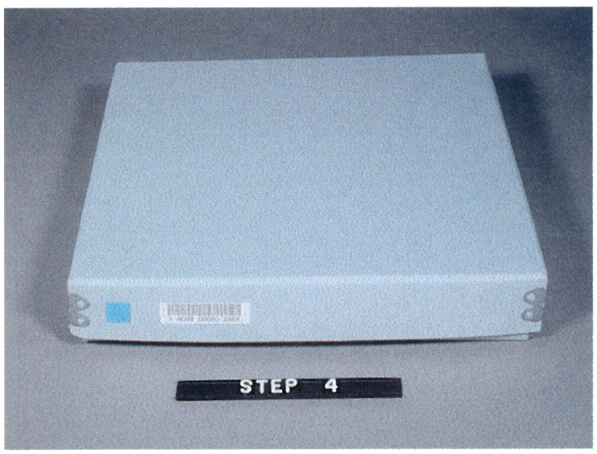
Film is inserted into low density polyethylene (LDPE) bag.



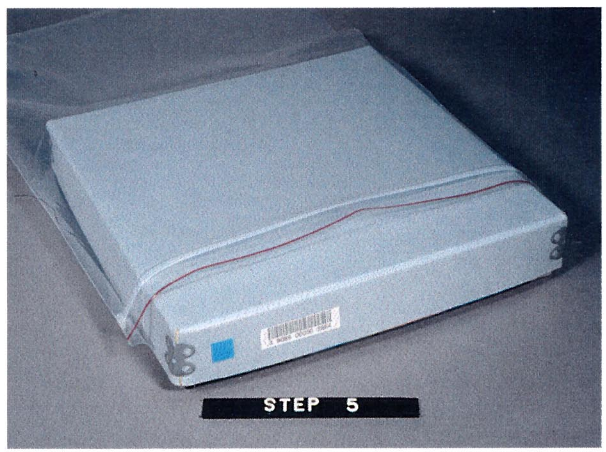
Bagged film is placed into film storage box.



Tyvek packets containing silica gel establish the desired shelf life.



Storage box lid is added. The cobaltous chloride moisture indicator is attached to the lid.



Outer LDPE bag is added and sealed.

Motion picture films stored in a standard laboratory grade freezer. The silica gel (approx. 50 grams) will last 20 years before it must be replaced.

Any freezer technology may be used. Shown here are Hussman Corporation modular reach-in units that can store 20,000 rolls of motion picture film.

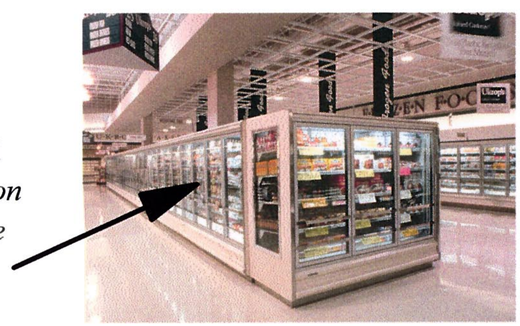


Figure 3.

Drying time for 4-ply mat board.

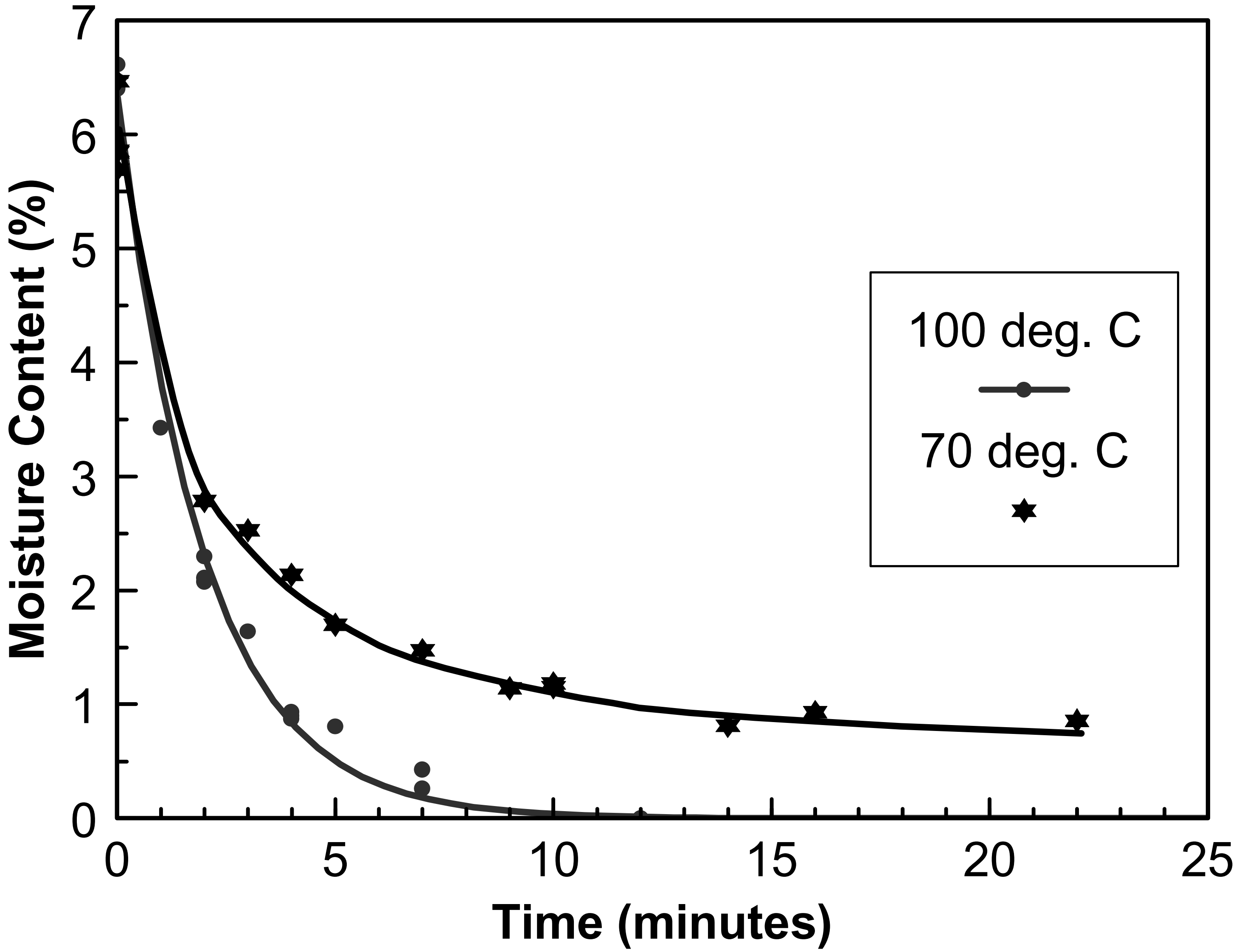


Figure 4.

Package shelf life: Moisture trap comprised of 2 sheets of 4-ply mat board enclosed within 4 mil thick LDPE at -18C.

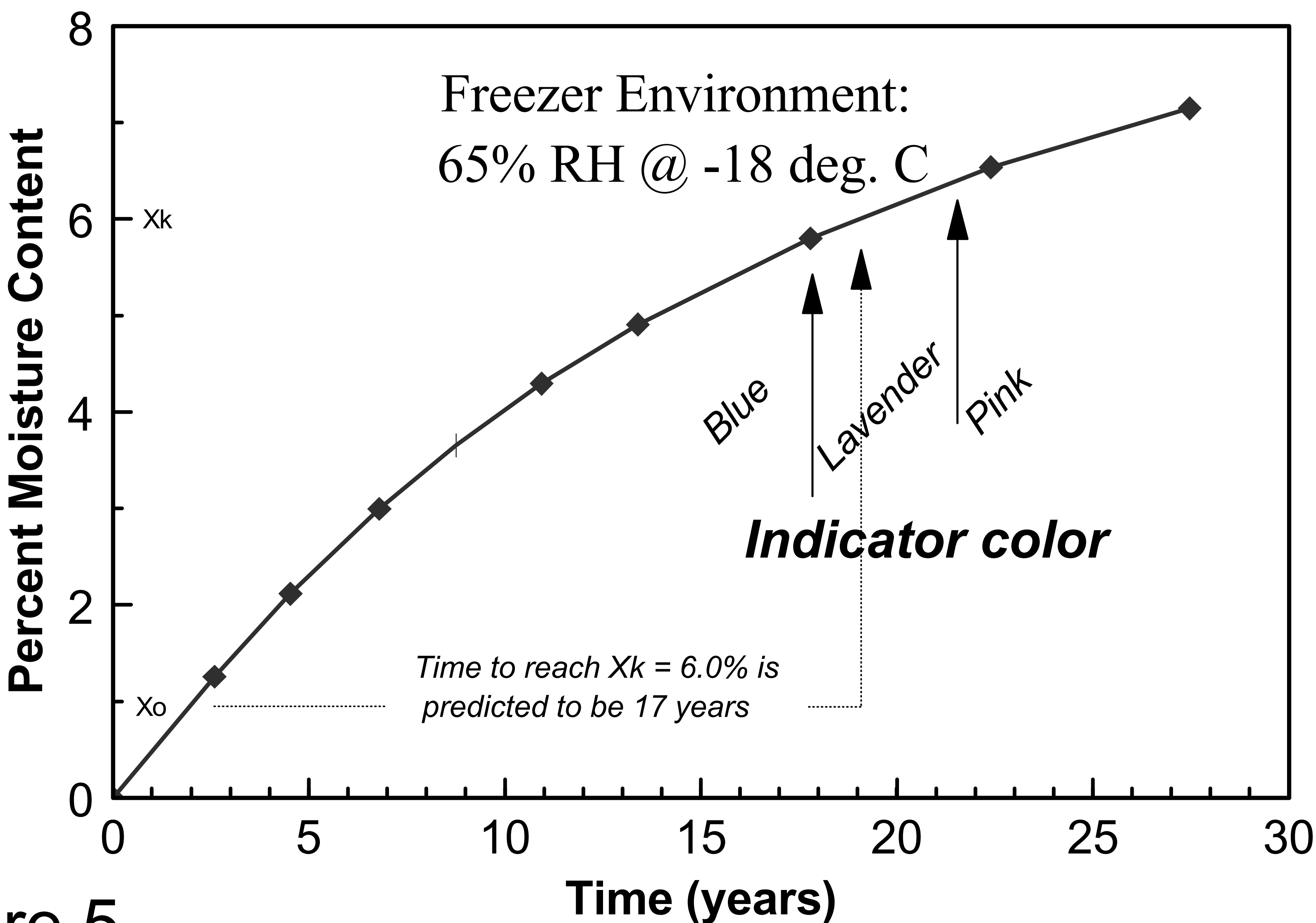


Figure 5.

Moisture Absorption Isotherm Data for Conservation Mat Board.

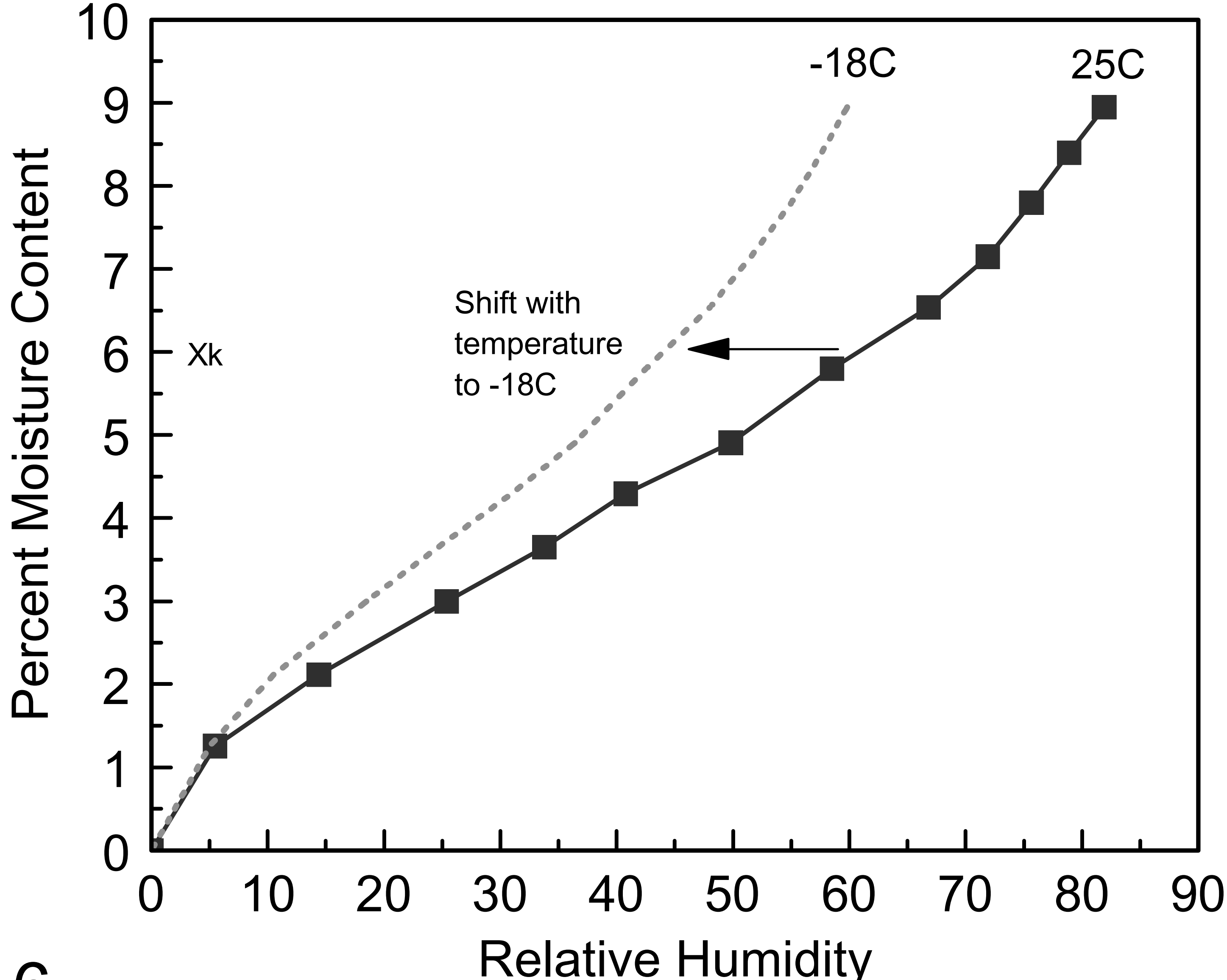


Figure 6.

Moisture Absorption Isotherm Data for Silica Gel.

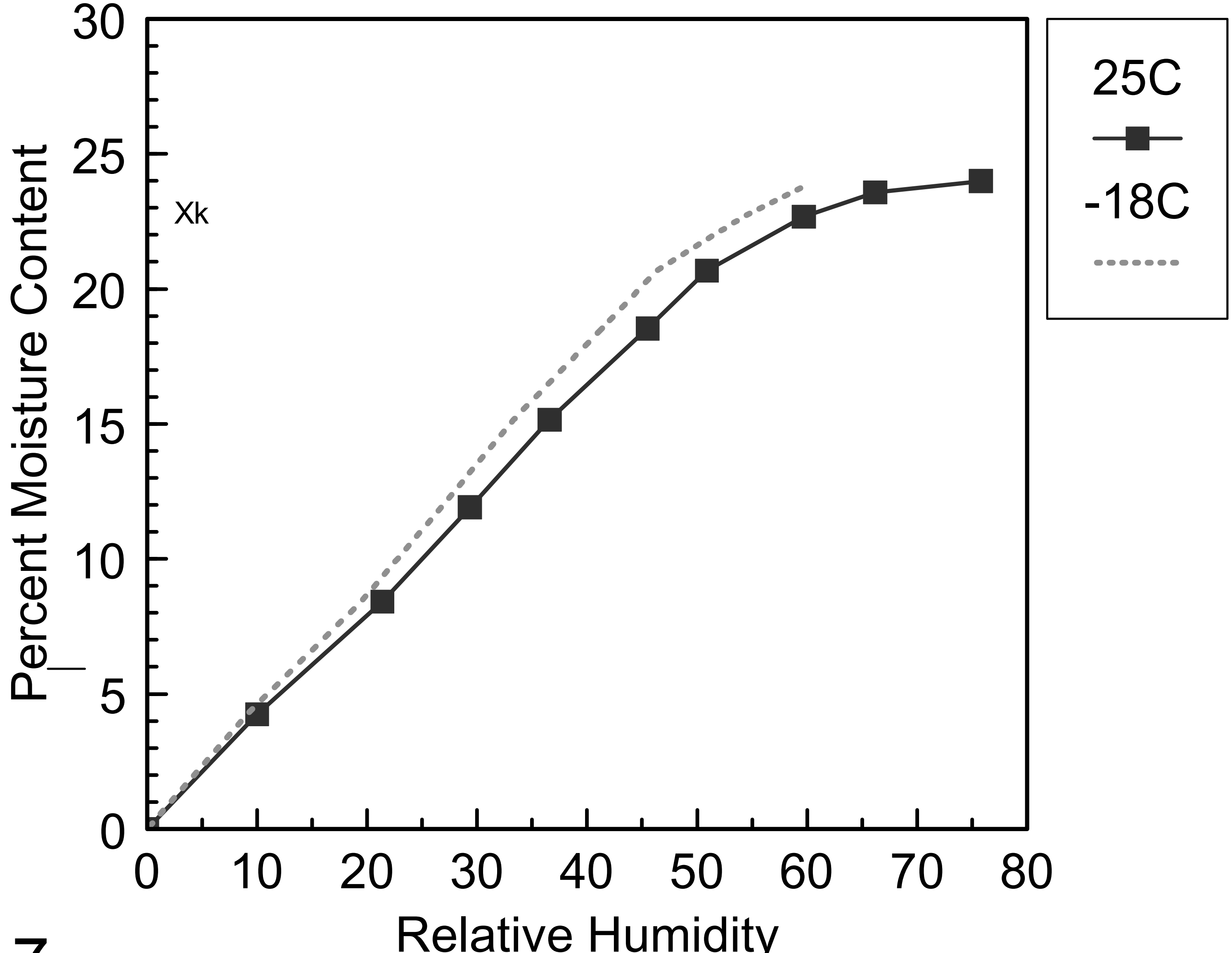
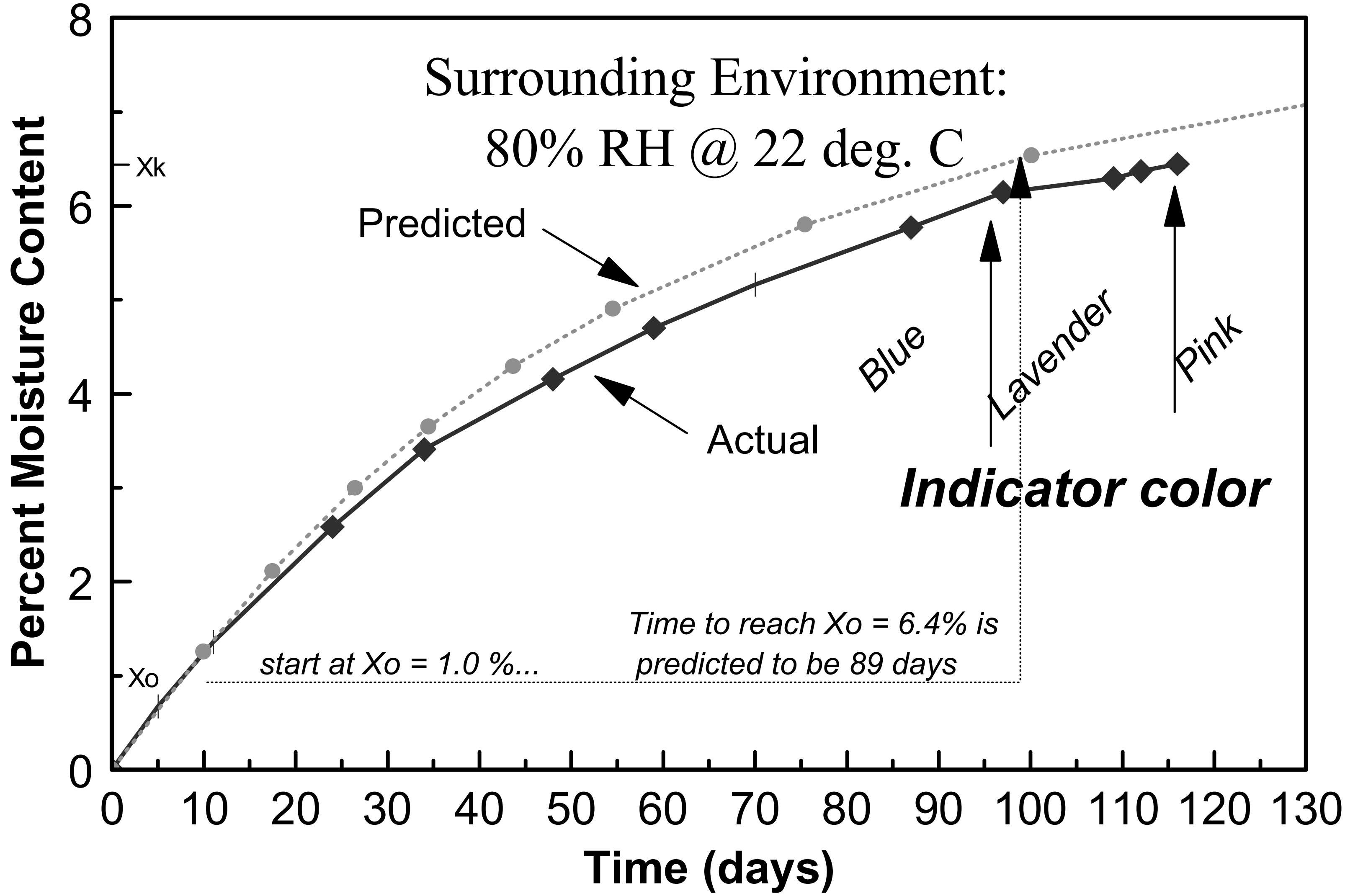


Figure 7.

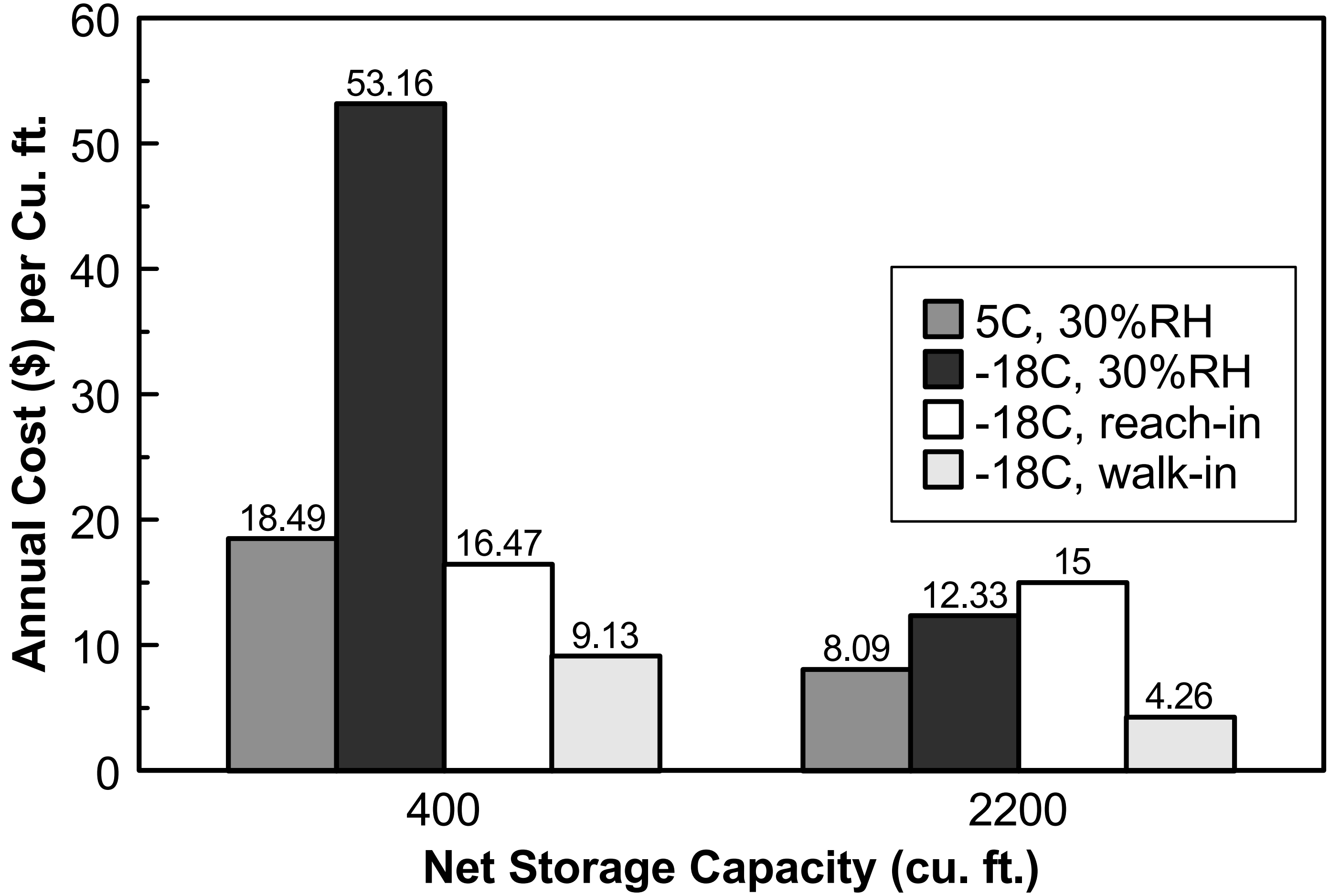
Package shelf life: predicted versus actual test results.



Note: In this test, a critical moisture indicator specified to change color at 65%RH@ 25 deg. C was used.

Figure 8.

Energy Costs for Cold Storage



For Walk-in vault design: 33% volume utilization factor, 85% shelf space utilization factor

For Reach-in freezer design: 80% shelf space utilization factor.:

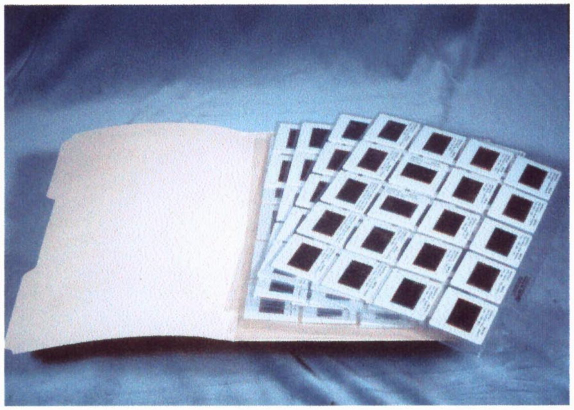
Energy cost = $0.10 per KWH:

Figure 9.

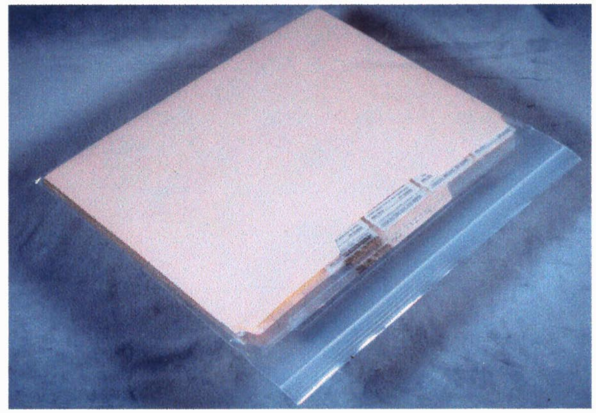
Rev: M.H. McC-G. 10/18/94

CMI Package Design

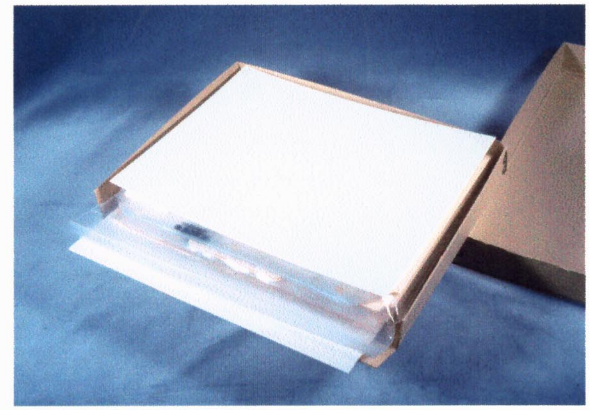
Drop-front Conservation Box Style



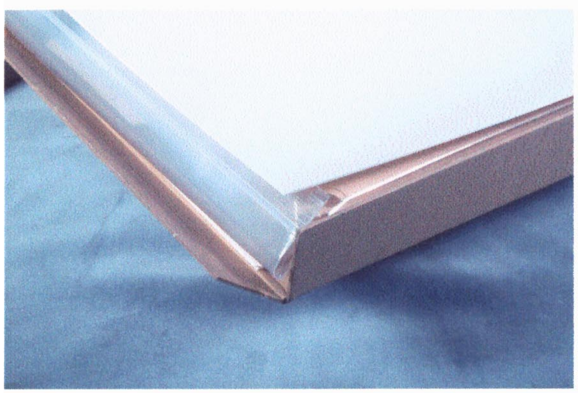
1. Photo materials are placed in standard-format plastic enclosures.



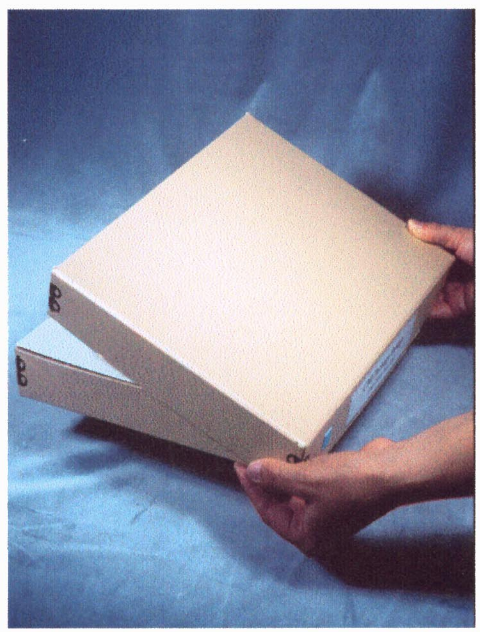
2. Enclosures and file folders are placed inside LDPE inner bag.



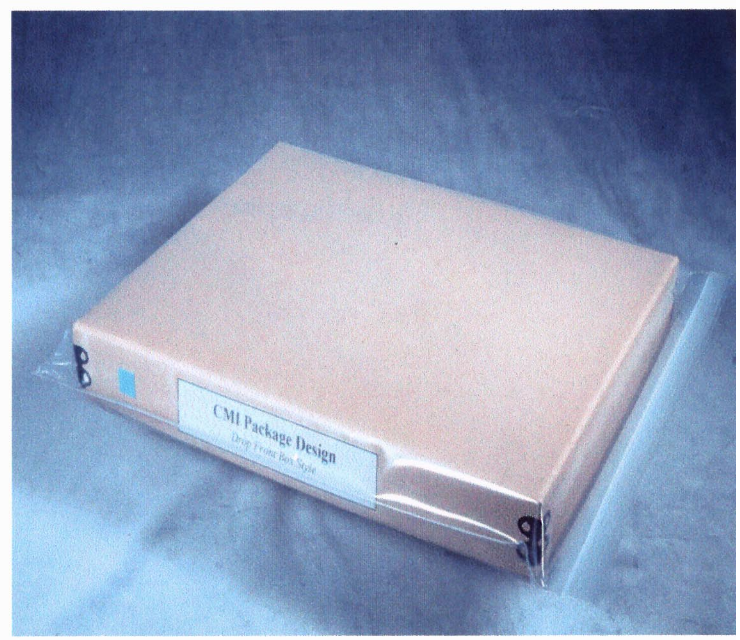
3. Dried mat board and inner bag is inserted into drop-front style box.



Close-up view of inner bag, mat board, and bottom of drop-front conservation box.



4. Box top is easiest to close by starting at the drop front.



5. Box is inserted into outer LDPE bag, and bag is sealed. Package is now complete.

Figure 10

Conserve O Gram

June 2001 Number 2/15

Cobalt Indicating Silica Gel Health And Safety Update

Standard indicating silica gel is often used within microclimates to control Relative Humidity (see *Conserve O Gram* 1/8). Cobalt is present in small concentrations (0.5 to 1.0% by weight) in indicating silica gel. As of July 1, 2000, British Chemical Regulations have required that indicating silica gel be labeled and disposed of as a hazardous material. While cobalt chloride has not yet been listed on any U.S.-based hazardous materials registries, its change in status suggests that this material should be treated with the same level of protection as is required elsewhere.

Health and Safety Issues

Cobalt is a skin and respiratory system sensitizer. It is a European Economic Community (EEC) List II substance for control of dangerous substances in the aquatic environment and must not be allowed to contaminate soil and water.
The cancer status varies on Material Safety Data Sheet (MSDS) reports provided by manufacturers and suppliers from "no reports" to "Cobalt and its compounds have been shown to cause cancer in laboratory animals." The threshold limit value (TLV) is 0.01 mg/m^3.

Although the concentration of cobalt is small in indicating silica gel, concerns revolve around the possible contamination of silica gel dust with cobalt chloride. There also are hazards stemming from the inhalation of silica dust.

Small RH indicating cards and test papers that turn from blue to pink also contain cobalt chloride. Since the danger is potential inhalation of cobalt dust, the use of these cards should not be a problem. However, if the card gets wet, there is the possibility that the cobalt chloride could migrate and recrystallize where it could conceivably become airborne.

Disposal of Silica Gel

All silica gel is listed as "hazardous waste" by the EPA (Resource Conservation Recovery Act) and must be disposed of appropriately. Cobalt from indicating gel could pose a greater hazard than standard silica gel as cobalt can leach into runoff or groundwater and poison aquatic life. Contact your park or regional HAZMAT coordinator to obtain information on appropriate storage containers and disposal instructions.

Alternative Materials

Sorbead Orange desiccant features a biodegradable, organic indicator (available from Engelhard Chemicals). The amount of indicator used in Sorbead Orange is five to ten times lower than the amount of cobalt chloride found in cobalt chloride indicating desiccants. It changes from bright orange to translucent in color when it has adsorbed approximately 6% of water by weight. This desiccant can be regenerated (returned to its original orange color and adsorption capacity) by heating to a temperature of 270-320ºF.

Another choice, manufactured by Kaltron Pettibone, is Silica Gel Yellow, an indicator gel with phenolphthalein (0.01% by weight concentration). It is distributed by Art Preservation Services. This indicator changes from yellow when dry to green, and finally to deep blue when the gel has adsorbed approximately 5% of water by weight. Heating temperatures for regeneration are the same as for most non-indicating gels, with a recommended range of approximately 300-350ºF.

Indicating silica gels will alert you when standard gel is nearing its saturation point, but they won't reveal the exact RH. Use a hygrometer to evaluate your micro-environment's climate.

Answers to Frequently Asked Questions

Has indicating silica gel (blue) changed?

No. Indicating silica gel (blue) is the same as it has been for the past 60 years. There has been no change in its formulation.

Is indicating silica gel a hazardous substance?

Indicating silica gel with cobalt chloride as the indicator is listed as a hazardous substance for disposal by the European Economic Community. Cobalt chloride has **not** been listed on any U.S.-based hazardous materials registries.

Has cobalt impregnated silica gel been banned from use?

No. Cobalt impregnated silica gel has not been banned from use.

Why should I take additional precautions with silica gel?

The dust from all types of silica gel is an irritant, and appropriate ventilation (fume hood or appropriate respirator) should always be used when working with the gel. Cobalt chloride could be a component of silica gel dust when you are working with indicating gel.

Are there special instructions for shipping silica gel?

Contact your park or regional HAZMAT coordinator for information on shipping containers for disposal. Silica gel is still classified as non-hazardous for transportation.

Recommendations

1. Substitute Silica Gel Yellow or Sorbead Orange desiccant for future purchases of indicating silica gel (see supplier list).

2. Begin phasing out and replacing cobalt impregnated silica gel.

3. In handling all silica gel take the following precautions:

   - Wear gloves, lab coat and safety glasses.

   - Work in a fume hood or wear an appropriate respirator with a HEPA filter (see *Conserve O Gram* 2/13).

   - Place silica gel in appropriate, well-marked containers and contact your park or regional HAZMAT Coordinator for disposal.

4. Work toward replacing humidity indicator strips with dial hygrometers, thermo-hygrometers, or dataloggers.

Further Information

Material Safety Data Sheets for Cobalt Chloride can be obtained at:<www.htbaker.com/msds/ c4928.htm.>

The International Chemical Safety Card for Cobalt (II) Chloride can be found at: <www.cdc.gov/niosh/ipcs/ipcs0783.htm>

Safe handling procedures for indicating silica get can be found at: <www.geejaychemicals. co.uk/cobaltchloride.htm>

Alternative Sources of Indicating Silica Gel

Sorbead Orange
Engelhard Chemicals
120 Pine Street, P.O. Box 4017
Elyria, OH 44036
(440) 329-2586

Silica Gel Yellow
Art Preservation Services
315 East 89th Street
New York, NY 10028
(212) 722-6300

This *Conserve O Gram* is adapted from "Health and Safety News," AIC News Vol. 26, No. 1, January 2001, with the permission of the American Institute for Conservation of Historic and Artistic Works, and the authors, Lisa Goldberg and Steven Weintraub.

Additional information provided by Fred Sterniolo, Environmental Protection Specialist, Hazardous Waste Management Program, Park Facility Management Division, National Park Service.

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