

# EXPLORATIONS OF THE ROLE OF HUMIDITY FLUCTUATIONS IN THE DETERIORATION OF PAPER

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## ABSTRACT

The control of relative humidity is generally recognized as an important consideration in the proper storage and display of paper materials. However, the amount that the humidity can fluctuate and the rate at which it can change without causing damage are still unknown. In this study, samples of cotton filter paper (Whatman No. 42) were held at room temperature in a chamber having a relative humidity that alternated between 25 and 75% every two hours. Papers were removed from this chamber at intervals and analyzed for chemical deterioration, discoloration and strength loss. After roughly 2200 humidity cycles, the paper had suffered a reduction in cellulose degree of polymerization to one-half its initial value, nearly its leveling-off DP, and its zero-span tensile strength had fallen to one-third the initial fiber strength. Chemical products were found to be consistent with a predominantly hydrolytic degradation. These results, and the course of the strength loss during degradation, suggest that the cycling humidity causes rapid stress-induced hydrolysis in this filter paper.

## INTRODUCTION

The conditions of storage and display of paper materials have long been accepted as major factors in the usable life-span of the item. The effects of heat and light exposure on the deterioration of paper are well known and can be controlled relatively easily in most environments. The effects of humidity on paper collections are not as well understood, although the dangers of humidity extremes (mold growth at very high humidity, cockling, curl and stiffening at very low humidity) are recognized. Maintaining a humidity within these limits is prudent, but the necessary degree of humidity control within those bounds is not known. Since very tight control of the relative humidity (RH) can be expensive, understanding the risks of paper damage from humidity fluctuations is important when investing in climate control systems.

There is evidence that humidity fluctuations may pose a risk to paper materials. In the paper industry, uncontrolled RH fluctuations are a known hazard to paper materials that will bear physical loads: cycling RH conditions can accelerate irreversible physical deformations (in a process termed 'creep') in products such as corrugated cardboard containers [1]. Laboratory studies of paper aging in cycling humidity at elevated temperatures have demonstrated accelerated fold endurance loss, acid build-up, and discoloration [2, 3]. Another probe of paper experiencing cycling humidity showed evidence of free radicals being produced as chemical bonds were ruptured [4]. Taken together, the available evidence only demonstrates the possibility that humidity fluctuations can cause paper damage; the magnitude of that risk for specific papers in specific environments cannot be estimated.

This study is intended to probe these risks of deterioration for paper stored at room temperature in a cycling humidity environment. In this initial experiment, samples of pure cotton filter paper were held at 23°C in a small chamber in which the RH was cycled between 25 and 75% every two hours. The sample papers were then periodically analyzed for chemical degradation, physical strength loss and discoloration. The changes produced in the papers in this study will provide a benchmark for future work exploring effects of more moderate cycling humidity conditions.

## EXPERIMENTAL

In order to characterize precisely the chemical nature of the cellulose and its degradation products, a pure cellulose filter paper, Whatman No. 42, was studied. It is made from cotton linters and is slightly acidic, with a pH of about 5, due to its carboxylic acid

content. Each sample set was cut from a single large-size sheet. The chemical analyses of the cellulose have been described previously [5]. Degree of polymerization (DP) was derived from the measured viscosity of a solution of the cellulose in cupriethylenediamine [6]. From the change in DP, the concentration of chain links broken, termed the scissions, was calculated. Oxidation measurements were carried out using the hydrazine method [7] to measure the carbonyl group concentrations and the standard methylene blue method [8] for the carboxyl groups. The carbonyl results listed are the average of two duplicate measurements. The cold-extraction pH was measured using the Tappi standard [9] with the modification of Scallan [10] in which 0.1M sodium chloride (NaCl) is used as the soaking solution rather than deionized water. Brightness of the paper sheets was measured using a Macbeth Color-Eye 7000 reflectance spectrophotometer. The color measurements are given in terms of percent reflectance at 460nm, which would show yellowing as a decrease in this value. The zero-span tensile strength was determined with the Pulmac Troubleshooter machine, and the results listed are the average of nine duplicate measurements. Prior to testing, the samples were held in the constant environment room at 23°C and 50% RH for a day to equilibrate.

Paper samples were exposed to humidity variations using a specially constructed apparatus that was set up inside a constant environment room. Pressurized air was purified by passage through a particulate filter, Purafil (potassium permanganate) and activated charcoal, then was dried thoroughly by passing through the desiccant Drierite (anhydrous calcium sulfate). The air stream was then divided into two parts, one of which was humidified by bubbling through deionized water. Metered flows of the dry and humid air streams were mixed to create the desired humidities, and solenoid valves controlled with a timer automatically switched the air flow that was fed into the sample chamber. The sample chambers were stainless steel and glass desiccator cabinets that were each outfitted with an air inlet and outlet, a fan for circulation, and a probe for monitoring the temperature and humidity. One chamber was held at a constant 50% relative humidity as a control check on the system. The other chamber had RH that cycled between 25 and 75% every two hours. With the flow rates used, the air within the chamber could be exchanged completely in about 30 minutes. Sample sheets were hung inside these chambers, with no more than four sheets exposed at the same time. In addition to the two sample sets exposed in these two chambers, a third set was kept in the constant environment room as a further control, and samples were tested at similar intervals as the other samples withdrawn from the chambers.

## RESULTS

The results of the exposure tests are summarized in Table 1. Figure 1 shows the scissions versus humidity cycles for the cycling humidity samples. After 10 weeks in the cycling humidity chamber, corresponding to 420 cycles of humidity, the sample papers experienced a sharp reduction in the DP of almost a third of the initial value. The degradation continued at a gradually slowing rate until, after 30 weeks, the DP approached the 'leveling-off' point that approximately represents the size of cellulose crystallites. The steady humidity samples were initially within normal variation in DP, but after 30 weeks there seems to

Table 1 Results of tests of filter paper exposed to a cycling or steady humidity environment at room temperature, or held in a constant environment room.

Humidity cycles	DP	Scissions, mmol.100g <sup>-1</sup>	Carbonyl, mmol.100g <sup>-1</sup>	Δcarbonyl mmol.100g <sup>-1</sup>	Carboxyl, meq.100g <sup>-1</sup>	pH	%R at 460nm	Zero-span tensile strength, kg.mm <sup>-2</sup>
<i>Cycling humidity samples</i>								
0	575	0	1.95	0	0.59	4.9	91.3	5.09
420	393	1.00	3.30	1.35	0.51			
840	314	1.78	4.18	2.23	0.52	4.8	90.2	2.54
1260	277	2.30	4.57	2.62	0.48	4.8	89.6	2.04
1764	272	2.39	4.46	2.51	0.50	4.8	90.2	1.80
2184	255	2.70	4.91	2.96	0.47	4.7	89.8	1.52
<i>Steady humidity samples</i>								
0 <sup>a</sup>	591	0	1.98	0	0.57	4.9	91.4	5.02
10 <sup>a</sup>	622	-0.11	1.84	-0.14	0.56			
20 <sup>a</sup>	556	0.13	2.16	0.18	0.57	4.8	91.4	4.56
30 <sup>a</sup>	496	0.40	2.06	0.08	0.56	4.8	91.2	4.37
42 <sup>a</sup>	481	0.48	2.25	0.27	0.57	4.8	91.1	4.22
52 <sup>a</sup>	450	0.65	2.31	0.33	0.57	4.6	92.2	4.13
<i>Constant environment room samples</i>								
0 <sup>b</sup>	568	0	1.97	0	0.60		92.9	
10 <sup>b</sup>	558	0.04	2.15	0.18	0.56			
15 <sup>b</sup>	572	-0.01	2.00	0.03		5.0	92.3	4.88
23 <sup>b</sup>	549	0.07	1.97	0	0.57	4.9	92.0	4.84
42 <sup>b</sup>	563	0.02	1.84	-0.13	0.57	5.0	92.5	4.68

(a) Weeks in chamber; (b) Weeks from start of experiment

be a small amount of degradation in these samples that is noticeable but far less than the deterioration in the cycling chamber. This is puzzling and may suggest that the chambers can begin to accumulate some degradation products or contaminants of some sort after a long period, despite the constant flushing of air through them. By contrast, the samples held outside the chambers in the constant environment room showed very little change in DP.

Concurrent with this significant loss of DP, the carbonyl content of the cellulose also showed a large increase (Table 1). In contrast, the carboxyl contents in the papers held in cycling humidity showed little change, apart from the slight decrease seen when small fragments are formed, which, because they are water-soluble, are not detected in the methylene blue analysis. Similarly, the pH measurements (Table 1) show a slight initial drop of about 0.1 unit but then have little further change. The reflectance measurements indicate that none of the samples discolored from exposure to cycling humidity at room temperature.

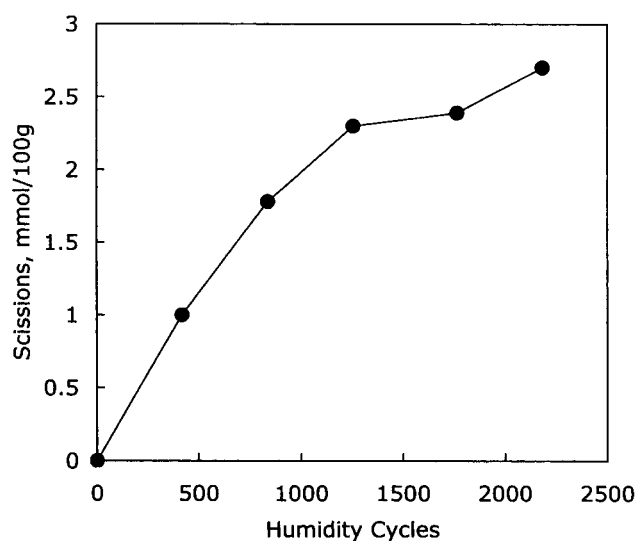


Fig. 1 Scission production in filter paper exposed to cycling humidity environment at room temperature.

The products of the degradation reactions can be quantitatively compared in order to determine the dominant mode of deterioration. This method, which is explained in detail in an earlier publication [5], compares the number of scissions produced to the change in carbonyl content. Hydrolytic reaction of the cellulose chain creates a new reducing end-group, an aldehyde which is counted as a carbonyl, every time a chain is broken. Thus, hydrolysis is indicated if the number of scissions is approximately equal to the increase in carbonyl groups. On the other hand, oxidative reactions tend to produce more carbonyls than scissions (for instance, in photodegradation reactions about 2.7 carbonyls are produced for every scission), and an excess of carbonyls over scissions is evidence for the involvement of oxidation chemistries in the deterioration.

Figure 2 illustrates this analysis, where the change in carbonyl content is plotted against the scissions for the cycling humidity

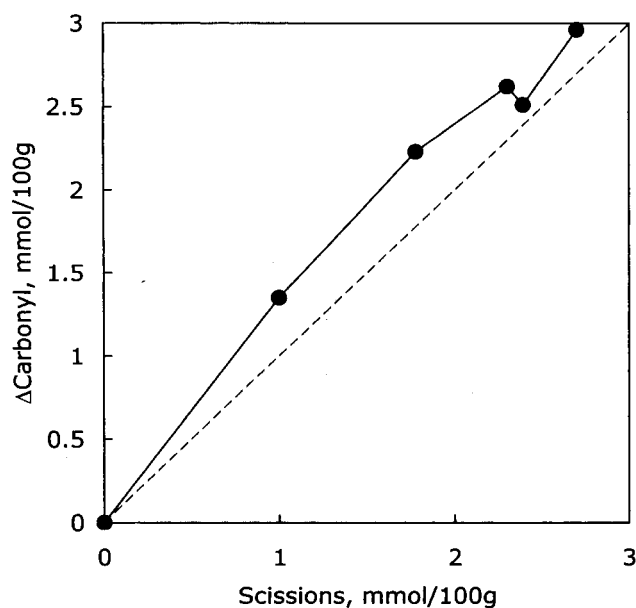


Fig. 2 Carbonyl versus scission production for filter paper exposed to cycling humidity environment at room temperature. The dashed line represents one carbonyl produced per scission.

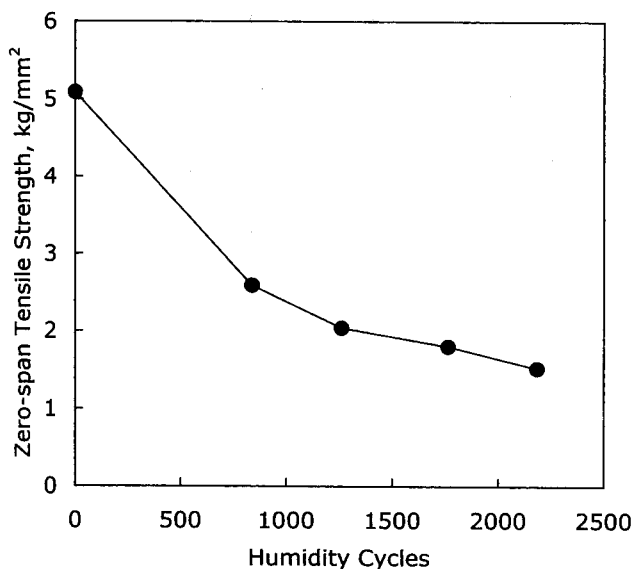


Fig. 3 Loss of zero-span tensile strength in filter paper exposed to cycling humidity environment at room temperature.

samples. The dashed line on this graph represents equal production of carbonyls and chain scissions, that is, the product distribution for hydrolysis. It can be seen that the experimental results are very close to this line throughout the exposure period. This product distribution, along with the lack of an increase in carboxyls or a significant decrease in pH, is consistent with the degradation of the cycling humidity samples being predominantly a hydrolytic reaction, with little or no contribution from oxidation processes, and this reaction occurs at a rate far greater than the hydrolysis of paper stored at constant humidity.

The zero-span tensile strength measurements for the papers exposed to cycling humidity are shown in Table 1 and plotted in Figure 3. It can be seen that the strength falls rapidly initially, slowing somewhat as the exposure progresses, until the sample sheets have lost nearly two-thirds of their strength and are extremely weak and brittle by the end of the test.

## DISCUSSION

In the present work, the accelerated loss of fiber strength in the paper stored in cycling humidity was very pronounced, with nearly two-thirds of the initial fiber strength having been lost by the end of the 52-week exposure (approximately 2200 humidity cycles). This strength loss results when the cellulose chains in the amorphous regions that tie together the cellulose crystallites and impart the cohesive strength to the fiber are broken. The measured decrease in the DP of the cellulose, to approximately half the initial DP, is roughly equivalent to one chain break per cellulose chain, and this amount of degradation could conceivably result in such a significant loss of cohesive strength.

In cycling humidity, such deterioration to the cellulose polymer is reasonably attributed to stresses exerted on the paper due to the physical distortions accompanying the gain and loss of moisture. Because of the complex arrangement of cellulose chains making up the fibers and of the fibers that compose the paper web, it is difficult to describe precisely the nature of those stresses, which could be either tensile, compressive or shear in nature [11]. Furthermore, it has been postulated that the suddenness of the humidity change could cause very high local stresses, as exterior portions of fibers react quickly to the new condition while interior portions are slower to respond. The resultant non-uniform moisture content and consequent fiber distortion are thought to create both shear forces within the fiber as well as very high tensile forces when physical loads become concentrated in

very small areas of the fiber [1, 12]. All of these forces can act to stress the fibers and the fiber bonds in the paper sheet, resulting in creep, strength loss and flexibility loss.

While it may seem unlikely that such physical stresses can severely weaken a strong, unrestrained cotton paper, several studies have demonstrated that these physical forces can be great enough to break chemical bonds that hold polymer chains together. Such mechanically induced polymer degradation, called 'mechanochemistry', has been widely studied in the polymer industry, both because it causes the erosion of performance properties during polymer processing and because the highly reactive broken chains can be further processed, in grafting reactions for example [13]. While mechanochemistry is often observed in polymers experiencing extremely high physical stresses, such as grinding, high-speed stirring or extrusion, evidence for broken bonds has also been obtained in paper that is simply humidified [4]. Apparently the mechanical action of the swelling or contraction of the paper web and fibers creates enough physical force to break chemical bonds in the material.

In cellulose chains subjected to stress, the chain is most likely to break at the weakest point, the oxygen link connecting the glucose rings. In most circumstances, the carbon-oxygen bond is severed so that free radicals are formed, with the carbon and oxygen atoms each carrying an unpaired electron that comprised half of the chemical bond between them. Such free radicals have been detected in a number of studies [4, 14-17], and their observation provides the most definitive evidence of mechanically induced bond breaking. Once formed, these radicals can also initiate oxidative reactions (production of peroxides, hydroperoxides, and eventually carbonyl or carboxyl groups) in the cellulose. These reactions have been exploited for creating branches or crosslinks or in grafting cellulose fragments to other polymers [13, pp. 168-169], and the triggered oxidation chemistries may also be involved in the discoloration phenomena that have been reported in papers experiencing wet-dry interfaces ('tidelines') [18] or cycling humidity at elevated temperatures [2, 3].

In the presence of water, though, it has been found that the mechanically induced degradation of cellulose can follow another path, namely, a hydrolytic breaking of the cellulose chain, and this can accompany the free radical oxidative reactions or become the dominant means by which cellulose chains are broken [13, pp. 296-302; 19]. This same mechanically activated hydrolysis has also been observed in other polymers that can experience hydrolytic chain breaking, such as polyesters [20, 21].

The exact mechanism by which tensile or shear stresses on a cellulose chain accelerate hydrolysis is not known. It is possible that coordination of water molecules at the stressed oxygen link will allow a more ionic bond breaking, creating the typical hydrolytic fragments when the bond finally cleaves, or that radicals produced when the bonds break further react to form products that resemble those of hydrolysis reactions (one carbonyl per chain break). It is also possible that physical stresses can simply distort the bond arrangement at a link that has an acid proton bound to the link oxygen (the initial arrangement in the conventional acid-catalyzed hydrolysis), stretching the link bonds or flattening the ring to more easily form the distorted conformation that is thought to be the transition state in cellulose hydrolysis [22].\*

While the literature describing the circumstances in which mechanically activated hydrolysis will dominate is sketchy, the

\*Cellulose chains under tension will probably react by extension and distortion of the link and ring bonds. It has been found that the rings are actually somewhat flexible [23, 24] but, unlike other glucose-based polysaccharides such as dextran or amylose, it is believed that cellulose cannot reduce tensile stresses through chair-boat reconfigurations of the glucose rings [25].

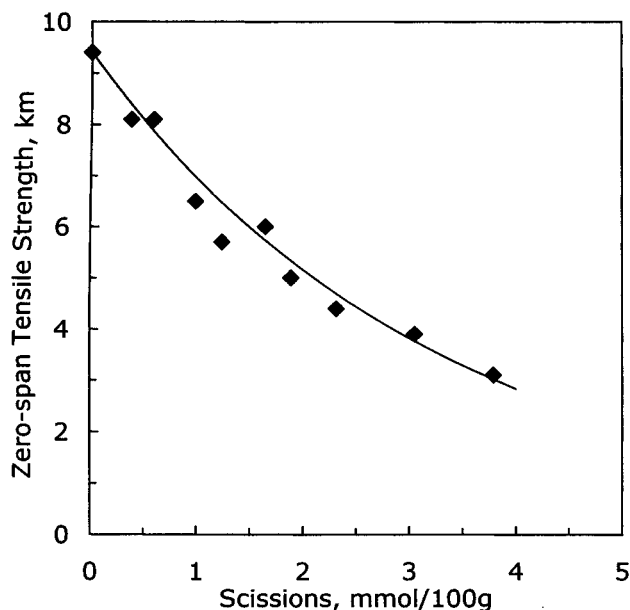


Fig. 4a Loss of zero-span tensile strength versus scissions produced in thermally aged cotton paper. Data from Zou *et al.* [27]. Note that scale is given in km of breaking length.

chemical analyses of the cellulose in the present study are consistent with hydrolytic degradation [5]. Other subsequent degradation reactions, such as oxidation of the many new aldehyde end-groups to carboxyls or their participation in chemistries that lead to discoloration, may still be possible, but these apparently were slow at the ambient temperatures used in this experiment.

Further support for this mechanically activated hydrolytic mechanism is provided by examining the efficiency of strength loss as the cellulose chains are broken in the cycling humidity environment. In normal cellulose hydrolysis (in an oven-aging test, for example) a large strength decrease is observed as the first cellulose chains are broken, and further chain breaking causes progressively smaller decreases in strength [26, 27]. The strength loss has thus been found to be roughly exponential with additional chain breaks. Figure 4a shows the results of oven aging of cotton paper published by Zou *et al.* [27]. This decreasing efficiency for strength loss occurs because, in an initially strong paper, there are many intact tie chains of cellulose linking the crystallites and providing strength, and the first scissions will probably break one of these tie chains and reduce the strength. As deterioration proceeds, however, there are fewer intact tie chains and the chances increase that hydrolysis will occur on a chain that has already broken, and is thus no longer linking crystallites and contributing to cohesive strength. Thus, the chain-breaking reaction becomes progressively less efficient at decreasing the strength [26, 28, 29].

The strength loss in the paper experiencing cycling humidity follows a very different course, shown in Figure 4b. Here, the efficiency of strength loss is unchanged over the course of the deterioration, with the later chain scissions creating just as large a strength decrease as the earlier ones. This is consistent with the mechanism of accelerated hydrolysis occurring on physically stressed chains. Only the load-bearing tie chains are likely to experience the physical stresses imparted by the humidity changes, and thus the mechanically activated hydrolysis is localized on the strength-contributing chains. As these stressed tie chains break, the load bearing shifts to other chains, which then experience the stresses of the humidity cycles. Thus, the mechanical stresses are always exerted on tie chains, and mechanically activated chain breaks will always result in strength loss.

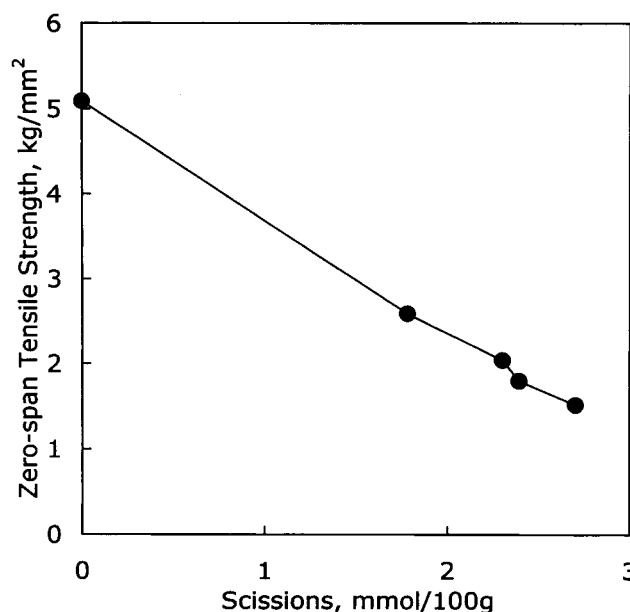


Fig. 4b Loss of zero-span tensile strength versus scissions produced in filter paper exposed to cycling humidity environment at room temperature.

## CONCLUSIONS

Filter paper exposed at room temperature to a cycling humidity environment experienced a large reduction in degree of polymerization (DP), as well as a very severe strength loss. Chemical analysis indicates a predominantly hydrolytic degradation. The rapid room temperature hydrolysis of this mildly acidic paper is believed to be induced by the physical stresses on the cellulose chains as they respond to moisture changes. This behavior is probably analogous to similar observations of accelerated hydrolysis observed in other studies of mechanically stressed cellulose.

Much more study is needed before these laboratory tests can be extended to recommendations for collection storage. Clearly the tests performed here were designed to explore extreme environmental conditions, and the probability that a paper material will experience a single sudden transition to an extreme humidity, much less several thousand consecutive ones, is very small. Cotton papers are rarely encountered in such weak condition, which argues against purely environmental influences having such a devastating effect. However, weak acidic papers are frequently encountered, and the deterioration is attributed to the acidity; brittle, discolored edges of book pages are observed, and the damage is attributed to air pollutants. It is not yet known whether humidity changes are also important factors in such cases, aggravating an existing acid-catalyzed hydrolysis problem.

Much remains to be learned about the risks from more moderate and less abrupt humidity changes, and about the risks to more or less acidic paper materials. Until such factors have been explored more thoroughly, it is premature to use the observations in this study to argue for specific collection environments. Nevertheless, one can add this environmentally induced hydrolytic deterioration to the list of processes that must be examined in more detail.

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## PRODUCTS

Drierite: W.A. Hammond Drierite Co. Ltd, PO Box 460, Xenia, OH 45385, USA, [www.drierite.com](http://www.drierite.com)

Macbeth Color-Eye 7000 spectrophotometer: GretagMacbeth LLC, 617 Little Britain Road, New Windsor, NY 12553, USA, [www.gretagmacbeth.com](http://www.gretagmacbeth.com)

Pulmac Troubleshooter tensile tester: Pulmac Instruments International, Box 50, HCR 34, Montpelier, VT 05602, USA, [www.pulmac.com](http://www.pulmac.com)

Purafil: Purafil Inc., 2654 Weaver Way, Doraville, GA 30340, USA, [www.purafil.com](http://www.purafil.com)

Whatman filter paper: Whatman Inc., 9 Bridewell Place, Clifton, NJ 07014, USA, [www.whatman.com](http://www.whatman.com)

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