ABSTRACT

The purpose of this report is to acquaint all personnel with some technical aspects of micrographics. The various film types used in the production of microfiche are discussed, including silver halide, diazo, and vesicular films. Other imaging systems used in micrographics are reviewed, and a basic introduction to sensitometry is given. The archival considerations of micrographics are explained in terms of their use properties and image stability, as well as prediction of image stability by chemical kinetics. The microfiche testing program currently underway at the Government Printing Office is reviewed, and recommendations for the use of the three primary types of film are offered. (PAO)
ARCHIVAL STABILITY OF MICROFILM --
A Technical Review

by

Albert R. Materazzi
ARCHIVAL STABILITY OF MICROFILM -- A TECHNICAL REVIEW

by Albert R. Materazzi
Manager, Quality Control and Technical Department

Introduction

Micrographics is a rapidly growing segment of the graphic communications industry. It is growing at a rate of 10-15 percent annually compared to the printing industry's 3.5 percent. While no one expects microfilm to completely replace paper, it has and will continue to impact printing and publishing--certain segments and certain products more than others. The Government Printing Office, its customers, and its contractors will be no exception. In a presentation to GraphCom, D. W. McArthur of 3M's Micrographic Products Division said:

"There is one area where there is a little conflict: Micrographics have, since their beginnings, performed a tremendous archival service -- allowing us to keep records of all kinds of documents for reference without drowning in a tidal wave of paper. It's when micrographics systems begin to take on the role we call active and vital that graphics people start to beat their plowshares into swords."

The purpose of this report is to acquaint all personnel with some technical aspects of this important communications technology.

Microfilm products offer several important advantages over printed paper products. In many instances they more than compensate for the inherent disadvantages of an unfamiliar medium which is inconvenient to use for the uninitiated. Among these are:

(1) Tremendous reduction in storage space. (95-98%)
(2) Relatively low reproduction costs. (1/5 to 1/6 of hard copy)
(3) Easy, high-speed distribution. (85% on mailing costs)

Distribution: T
Microfilmed products can also be produced from data stored in computers (COM or Computer Output on Microfilm). This is particularly useful for products which need not be produced in printed form and which are intended primarily for reference purposes. It is also possible to record on microfilm the image on the cathode ray tube of an electronic photocomposition device such as GPO's Video Comp 500's, again bypassing the printed product. This attribute is most useful for parts lists, inventory lists, directory lists, etc.

GPO does not have microfiche reproduction facilities, and all fiche distributed are commercially procured under specifications generally used throughout government and industry.

Types of film employed:

Silver Halide. Because of their photographic speed, silver halide films are almost universally used for original recording. Used as such, they are non-polar, i.e., negative from a positive. Polar silver halide films (negative from negative) are also widely used in duplication.

A suitably transparent plastic film, usually a cellulose ester (e.g., acetate) or polyester (e.g., polyethylene-terphthalate trademarked "Estar" or "Cronar") is coated on one side with a gelatin emulsion of silver halide (bromides, iodides, or chlorides). The emulsion is specially ripened (aged) before coating it so that it will produce extremely fine grains of metallic silver and thus obtain good resolution. The emulsion can also contain sensitizing dyes since silver halide is normally only sensitive to the ultraviolet and blue components of the spectrum. The reverse side of the film may be coated with gelatin containing an anti-halation dye which prevents actinic light (i.e., light which will have a photographic effect) from being reflected back into the photosensitive layer and blurring the image. The gelatin also prevents the film from curling as would happen if only one side was coated.
Upon exposure to suitable light, a few molecules of the silver halide salt are reduced to metallic silver and free halogen. In a closed system, the action is reversible; and, indeed, when extreme amounts of light are used, silver halide will solarize, i.e., additional exposure will reduce the number of metallic silver particles formed; this is why greatly overexposed film can be less dense than that which is properly exposed. Photographic emulsions which can solarize easily are fogged chemically or by preexposure so that it is impossible to obtain a negative image. These types of emulsions are employed in duplicating films. Such films are used in making second-generation duplicates from the original masters.

Silver halide photographic systems are unique in that the effect of light can be multiplied many times by immersing the film in a bath containing a reducing agent (developer). This will selectively reduce the silver halide in situ wherever the exposure formed free silver. The developing bath contains, in addition to reducing agents, mild alkalis to control the pH and swell the gelatin, thus permitting the solution to diffuse uniformly throughout the layer. It also contains restrainers to prevent the unexposed portions from being affected. When the optimum amount of silver in the image area has been reduced, the action of the developer is neutralized in a weakly acid stop bath; and, then, the image is "fixed" by immersing it in a solution containing a chemical which will dissolve the silver halide, e.g., "hypo" (sodium thiosulfate). The fixing bath also contains materials which will harden the swollen gelatin and reduce the possibility of it being scratched or otherwise damaged. The film is then washed until most of the chemicals have been removed. The diffusion out of gelatin by washing is exponential. For example, if 90 percent of the salt is washed out in 5 minutes, then 10 percent still remains; another 5 minutes wash will remove 90 percent of these, leaving a residual of 1 percent, and so forth. Theoretically, the salt concentration will never totally disappear. The aspects of fixation and washing of silver halide-gelatin emulsions was studied by Green. He furnished data which can be used for optimum fixing and washing with the most economical use of chemicals and water.
Standards and tests have been established by the American National Standards Institute for determining maximum amounts of thiosulfate which can remain in films destined for archival storage. Not only does the thiosulfate remain in the non-image areas of the film, but it is strongly absorbed by the silver comprising the image left there. In time it will form yellow silver sulfide and damage the film. For greater archival stability, silver microfilm can be gold toned. While the technique is well known, we do not know how often it is used in actual practice.

Normally processed first-generation silver halide films are non-polar (negative), i.e., light portions on the original are dark on the film, and vice versa. Silver halide second-generation films will be positive, but there is an image definition loss of up to 20 percent. Third-generation films made from this positive would result in negatives, again with a possible 20 percent loss.

However, it is possible to process silver halide films by reversal chemistry, in which case they would be polar (i.e., positive from positive or negative from negative). In reversal processing, the film is not fixed after development but, instead, immersed in a bleach which converts the metallic silver to a complex which is not light sensitive. The film is then reexposed and redeveloped, forming metallic silver in the image areas. It is then fixed, at which time the silver complex comprising the original image is removed. The film is then washed. Reversal processing does result in some loss of contrast. This type of processing is used for the film exposed in GPO's Linotrons and VC 500 electronic phototypesetters.

If properly processed and stored, silver images will last a long time. The film must be fixed completely; otherwise, non-image areas will darken and result in loss of contrast. If all of the processing chemicals are not removed, the metallic silver will react with them and fade badly. Examples of this have been experienced by all of us, particularly with quick-processed
photographic prints. Silver is also a reactive metal and combines easily with atmospheric contaminants such as halides, sulfides, hydrogen peroxide, sulfur dioxide, etc. Gelatin is subject to bioattack from bacteria, molds, and vermin, particularly under conditions of high heat and humidity. The effect of fungus on silver gelatin, diazo, and vesicular films has been studied by Dorfman. Under test conditions he found heavy damage on silver gelatin films but not on diazo or vesicular.  

The hardness of gelatin is a function of temperature; it softens and will melt at about 90°C. Consequently, when handled at elevated temperatures, the film can be easily damaged (see below). Fingerprints must be removed immediately; otherwise, the salts they contain will react with the silver, damaging the legibility of the film. The silver halide image can also be affected by certain substances contained in packaging materials in which the film is stored. For this reason film destined for archival storage must meet very rigid standards.

The National Archives and Records Service has proposed a rule for micrographics management. The proposed rule rigidly prescribed the film processing, and packaging in addition to storage conditions. A most important provision of these proposed rules is that the master fiche can only be used for making duplicates.

Silver halide archival film must be stored in environmental conditions where the relative humidity will be in a range of 20 to 40 percent, and changes will not exceed more than 5 percent in a 24-hour period. Dehumidifiers using dessicants will not be used. The temperature will not exceed 21°C (70°F); and rapid, wide-ranging changes will be avoided, not to exceed 5 percent change in a 24-hour period. The ambient air will be filtered to remove dust particles which can abrade the image. Gaseous impurities will be removed by suitable washers and scrubbers.

**Diazo**

The photosensitive system in diazo systems is completely different. A variety of chemicals are lumped under the term "diazo,"
derived from the French word for nitrogen, "azote." As can be expected, not all diazos undergo identical reactions. Any substance which contains the diazo group (-N=N-) in its molecule is properly called a diazo. These materials are very unstable; if not properly stabilized, they can explode violently. However, they can be stabilized by forming salts with metal chlorides (e.g., zinc or cadmium), fluoroboric acid, etc. Dissolved in a suitable resin binder, it is in this form that they are used in diazo films. During exposure, the diazo nitrogen will split off leaving a colorless material behind. Like most light-sensitive compounds, they are sensitive only to light in the blue and UV regions of the spectrum. Immediately after exposure, there is a faint image visible which consists of the original diazo. To be useful, it must be "developed."

Diazro compounds will "couple" with a variety of organic chemicals to form highly colored azo dyes similar to those which have been in use in the textile industry for years. Azo dyes are also absorbed on inert materials to form pigments used in paints and printing inks. The developed diazo image is an azo dye.

Diazro films which are to be used in microfilm contain a suitably stabilized diazonium salt and one or more coupling agents which will form a dark composite image. The mixture is coated on the film in a resin which forms a tough film when dried. Upon exposure, the diazo component is decomposed in light struck areas, and the decomposition product will no longer couple. The coupling reaction takes place best under alkaline conditions; so, after exposure, the film is placed in an atmosphere of ammonia vapor. It is simultaneously "developed" (image is colored) and "fixed" (no longer light sensitive). Heat can be used to develop and fix some types of diazo. Such films are called "Termal Diazo."

If the exposure has not been sufficient to destroy all of the diazo in the non-image portions, that which remains will darken in time, reducing the overall contrast, especially if it is not properly developed.
Under certain conditions (e.g., at elevated temperatures), the residual coupler and some of the reaction products of the light-induced decomposition of diazos left in the non-image areas can react with substances in the atmosphere and oxidize to a brownish color, reducing the overall contrast.

Being organic, azo dyes can be expected to fade, even in the dark, particularly if they have not been properly stabilized. It should be noted that the azo dyes which form the image are far less sensitive to light than the original unexposed diazo compounds. All colored materials absorb certain portions of incident light; and, over long periods, may fade as a result.17/ Since the shorter wavelengths have the most energy stability, they can be increased by protecting the materials from UV rich sources, e.g., overcoating with a transparent film containing a UV absorber, allowing light to reach the image through the film base or interposing UV filters between the film and light source.

Heat can also decompose diazo compounds, but the chemical reactions are different for heat and light. In his book, Dr. Jaromir Kosar states, "In this connection, it is of interest to note that the stability of diazo compounds does not always go hand in hand with their light sensitivity; in other words, there is no direct relationship between light sensitivity and thermal stability."18/ This also applies to the azo dyes comprising the image.

The photographic speed and contrast of diazo materials is directly dependent on their concentration in the coating; the more diazo, the slower the speed, and the more contrast possible. Therefore, real dark images can only be had at some loss of speed. Generally, the darker the image, the longer it will take for a diazo image to fade to the point of unusability.

The light decomposition of organic dyes follows the laws of photochemistry. Most important, for light to have an effect, it must be absorbed. Thus, red light illuminating a red substance cannot fade it since it would all be reflected or transmitted. Secondly, as light proceeds through a transparent
colored material, it is attenuated and only the molecules nearest the light source get the full amount of the energy contained in the incident light. Therefore, fading in microfilm can be controlled to a certain extent by intelligent use of ambient light conditions during use.

Diazo films have several important advantages. They can be dry processed in line with the exposing light, they cost much less than silver films, and they have higher resolving power than silver permitting more faithful duplicates to be made. They are polar, i.e., a positive results from a positive or a negative from a negative. Thus, the original silver negative need only be used once to form a diazo duplicate from which any number of other duplicates can be formed. There is only 4 percent loss in image fidelity when copies are made compared to the 20 percent loss when silver halide films are copied. Diazo images are nearly grainless, permitting larger reproductions without grain interference. The tougher resin coating will withstand more handling without damage than gelatin, and it is not subject to biological attack. Because of dry processing, the film can be mounted in aperture cards prior to exposure. Finally, "the diazotype image, when properly processed and stored, is, contrary to general opinion, quite stable and will last for more than 50 years, which is longer than is required by most applications."

Vesicular Film. In addition to silver halide and diazo, vesicular films are widely used in the manufacture of microfiche. The word, "vesicle," means a small spherical cavity in volcanic rock which was produced by bubbles of gas in the molten rock. The word was first used in photography in a 1932 Kalle patent which described a system in which nitrogen bubbles may form whenever diazonium salts are exposed to light. This effect can be intensified by a subsequent exposure to heat or steam forming an image composed of bubbles; the extent depends upon the medium in which the diazo salts are contained.
Commercial vesicular imaging films date from 1952 with most of the early research and development being conducted by the Kalvar Corporation. Since then others have entered the field; the best known of which is the Xidex Corporation. The vesicular imaging system consists of a stabilized diazonium salt, molecularly dispersed in a polymer layer. These are decomposed upon exposure to ultraviolet light, giving off nitrogen gas. Immediately upon formation, it is under high pressure because it is confined by the polymer. Left to itself the gas would eventually diffuse out, but for a short period after exposure it is a latent image. If the film is heated during this period, the polymer softens and the gas expands forming vesicles of from 0.5 to 2 microns in diameter. When the film cools, the polymer forms crystals at the boundary of the vesicles. In exposed areas, you now have millions of permanent small bubbles or vesicles. The film is fixed by reexposing to light and allowing the gas formed to escape normally.

Light impinging on the vesicular image is scattered (reflected, refracted, and absorbed) in proportion to the number of vesicles thereby producing a grey scale. The unique feature of vesicular images is that the apparent density is determined by the light collection cone angle. In other words, the smaller the opening in the imaging optics (i.e., f stop) the less light will be collected, and the greater the contrast in the resulting image. Figure 1 graphically shows the difference between light absorption which occurs in silver and diazo films and light scattering as occurs in vesicular films.
Vesicular films are non-polar, although techniques do exist which will reverse the polarity. They can be exposed and processed faster than all other duplicating films. Their contrast and resolution are adequate for most purposes, and they are economical.

Their growth initially was slowed because early vesicular films gave off hydrogen chloride, a highly corrosive gas which attacked file cabinets and containers. This has been corrected. Also, because of the fact that they scatter light, duplicates from it are not as easy to make as from films which absorb light. Special equipment is required.

Still, this type film is economical and finds many uses for source document duplication. It is the film used in the ERIC program (Educational Resources Information Center).

Obviously, anything which will damage the vesicles can damage the film. The worst offenders are sharp local pressure and heat. The longevity of vesicular films depends upon avoiding these two factors.

Other Imaging Systems Used In Micrographics

Silver halide, diazo and vesicular films are the primary duplicating films used in the manufacture of microfiche, the format used by GPO. There are a number of other less conventional micrographic systems used for specialized purposes. At present they are either too expensive or not sufficiently advanced for GPO applications. A brief mention of the more important ones should be made in a tutorial study such as this one, particularly since some of them show "archival promise."

Those receiving the most attention are the so-called "updatable" or "add on" microfilms which, as the name implies, permit updating of film files photographically. Previously, this had to be done mechanically, stripping new file entries into the existing rolls or fiche. The add-on capability is of tremendous value for active files but of less value to seldom used reference files containing fixed information.
Initially, the approach was to use photochromic dyes such as those used in National Cash Register's PCMI (Photochromic Microimaging). The image in such films is formed upon exposure, no development is needed. The unexposed areas remain light-sensitive and, if protected from actinic light, can be exposed at a later date. Because the image is molecular, such films have very high resolution and are used in ultra microfiche where the image is greatly reduced—up to \( \frac{1}{25} \) of the original size.

Latest developments involve electrostatic (Xerographic) imaging, the same basic photo mechanism used in the familiar Xerox \( ^{\text{TM}} \) and RCA's Electrofax \( ^{\text{TM}} \) licensed copying machines. In such systems, photo conductors such as selenium, zinc oxide, or various organic compounds, coated on suitable substrate are charged electrostatically. The charge is dissipated upon exposure to light; it remains in image areas and can be toned, dyed, or manipulated in various ways to produce an image. Obviously, for use in film systems, the photo conductors must be transparent.

On the market since 1973, the A. B. Dick/Scott System 200 is probably the most advanced. The film used is Scott's TEP (transparent electrographic film), the essential element of the system. It consists of a film base coated with a transparent organic photoconductor. It is charged, exposed, and toned in special equipment. The image polarity is positive and non-erasable. Unused portions of the film can be subsequently imaged as needed. \( \frac{1}{25} \) It is finding application in insurance, banking, medical, land title, and general business records.

A similar material is Coulter Systems's "K-C" film. In this case, the photoconductor is cadmium sulfide which imparts a yellowish cast to the film. A system for microfilm application is under development. \( \frac{1}{25} \frac{1}{21} \)

"Ovonic" film is yet another electrostatically imaged duplicating film. It was developed by Energy Conservation Devices for 3M's MicroOvonic File System and is officially designated as MOF-X1. It consists of a vapor coated metallic-like substance on a polyester film base. The inventor, S. R. Ovshinsky, calls these substances "amorphous semi-conductors." \( \frac{1}{25} \) The film is imaged by exposing to
high intensity light and requires no chemicals to process. It has positive polarity. Because the film is not affected by ambient light nor heat, additional or revised documents can subsequently be recorded on the exposed frames.  

Photo-deformable plastic film is another imaging system based on electrostatic technology. These thermoplastic photoconductive polymeric films are charged by corona discharge in the dark. An imagewise array of charges remains after exposure to a suitable subject. The film is now heated until the thermoplastic layer is molten; it will then deform in accordance with the pattern of charges. Remelting of the material erases the image, and the film can be reused. A product of this type is marketed by Microx Corporation. The technology was originally developed by General Electric. Earlier films required special viewing devices, but a revised version that can be used without a special system is in test market. Xerox reported on a similar technique which it called "Charge Transfer Frost Xerography" but has not commercialized on it to date. The whole subject of deformable films has been reviewed by Gaynor, formerly with General Electric and later with Bell and Howell. 

Thermally developed diazo films have been mentioned previously. Based on diazonium chemistry, they only require exposure to light and are developed by carefully controlled heat.  

Similar in use, but based on silver technology, are the so-called "dry silver" films, also known as photothermographic. Dry silver is a photographic process that enables the user to obtain a useful image by exposure to a visible light pattern and heat development. There are no chemicals used and nothing is destroyed or removed in processing. As in most photographic processes, light striking the coating forms an invisible latent image. When heat is applied, the chemicals contained in the coating, catalyzed by the latent image, form the developed silver images. The process is a negative acting system (sign reversing) providing good contrast, fine-grained silver images.
Basic Sensitometry

In order to completely understand photographic systems and how they are measured, some understanding of basic sensitometry is needed. For a complete treatment of the subject, the reader is referred to any text on photography. J. L. Tupper has an excellent review in Chapter 19 of Mees & James "Theory of the Photographic Process."

Photographic exposure is defined by the equation:

$$E = I \cdot T$$  \hspace{1cm} (1)

where $I$ is the intensity of the light reaching the photosensitive material measured in watts or ft candles, and $T$ is the time (measured in seconds) that the light is allowed to react. This is only true within broad limits. Most photosensitive materials demonstrate a reciprocity law failure, some more than others. For example, from equation (1) the photographic effect of 1,000 watts exposure for one second should equal that of 1 watt exposure for 1,000 seconds; but, in actual practice, this is not true. Secondly, there is an intermittency effect. Again, from equation (1) 100 exposures of 1 second each should yield the same effect as 1 exposure of 100 seconds, assuming equal intensity of light in both cases. And, again, this is not the case in actual practice.341

Because of these two effects, the use of a constant intense light to simulate numerous small exposures is not always valid. Several librarians have reported "fading" after exposure of diazo microfiche to "printing" lights or sunlight for long periods. Lights used in printers are intense and rich in ultraviolet (compared to those used in readers) because they are designed to expose comparatively slow duplicating films, e.g., diazo and vesicular. In addition, such lamps generate considerable heat. Heat and light on diazo films at the same time appear to have a synergistic effect, particularly under conditions of high humidity. Thus, it is not valid to equate a single long exposure to intense light with either: (1) exposure to low intensity lights found in readers, or (2) to numerous short printing exposures when the film is being duplicated.
The effects of exposure are studied by plotting the resulting density against the logarithm of the exposure. Characteristic "S" shaped curves result from which many photographic properties can be deduced; for example, photographic speed and contrast (Figure 2).

Density is defined by the equation:

$$D = \log \frac{1}{T} \quad (2)$$

where $T$ is the percent transmission of the incident light. Obviously, the more light transmitted, the less is the density. Thus, a photographic density of 1 means that the film is passing 10 percent of the light; 2 equals 1 percent transmission, and 3 equals 0.1 percent transmission. It is evident that at the higher densities contrast is greatly reduced. In other words, the contrast at the dark end of a grey scale is less than at the light end. For example, the difference in light transmission between a density of 0.5 and 0.6 is 6.5 percent; but, between a density of 0.9 and 1.0, it is only 2.6 percent, and between 1.9 and 2 it is 0.26 percent. Consequently, the equivalent reduction of density in the dark areas is not as serious as it would be in the light areas as far as readability is concerned.
Density is measured under two conditions identified as *visual density* and *printing density*. The term *visual* is used to indicate that the receiver of the transmitted flux is, or has, a spectral sensitivity equal to that of the eye. Similarly, the term *printing* is used to indicate that the receiver of the transmitted flux (i.e., the duplicating film) is, or has, a spectral sensitivity equal to that of a photographic printing material. In both cases, the spectral energy distribution of the incident flux is that of a tungsten lamp operated at a color temperature of 3000°K.

The term "contrast" has two meanings in photography. First, it is used as an expression to denote the rate of density change per unit exposure; it is expressed as the tangent of \( \theta \), the angle formed between the slope of the characteristic curve and the abscissa, and is referred to as \( \gamma \) (gamma). "Contrast" is also used to express the relationship between the high (D max) and low (D min) density of a photographic image, in this case it is referred to as \( \Delta D \) (delta D). When copying documents, \( \Delta D \) is determined by the amount of light reaching the film as reflected from the type and background of the copy. The contrast of the film is determined by the contrast of the document being copied. This poses a big problem when poorly typed letters on aged paper are being copied. Fortunately, it is not a problem with GPO produced documents since quality standards established for printing insure good original negatives.

The visual and printing densities of vesicular films (which scatter light instead of absorb it) cannot be measured in an ordinary densitometer which operates by measuring the amount of light absorbed; the instrument must be specially modified.\(^{36/37}\) Images on Photodeformable plastic films, on the other hand, refract light without change in optical density. The sensitometry of photo plastic films has been studied with modulation efficiency measuring apparatus by Aftergut and his associates at General Electric.\(^{38}\)

**The Meaning Of Archival Quality**

Obviously, the stability of documents entrusted to their care is a proper concern of librarians. There is probably no topic which will generate as much heated discussion among them as the use of the word "archival." This applies especially
to microfilm products since products printed on paper can always be "library bound" to increase their longevity, whereas librarians can exercise very little control over microfilmed products. The word "archival" is an adjective, the dictionary meaning of which relates it to a place where public records or historical documents of permanent value are preserved. Thus, the term "archival quality" applies to a document suitable for preservation in an archive. While an inference exists that it will have to be permanent, there is no period of time specified for which it must be usable.

Conditions of storage have been specified for archival libraries. Reference has been made previously to a proposed rule by NARS. It specifies silver halide films and, in fact, would prohibit storage of non-silver films in the same rigidly controlled room. ANSI has two standards for film storage which also specify ambient conditions:

PH1.41-1973, Practice for Storage of Processed Safety Photographic Film Other Than Microfilm; and

PH5.4-1970, Practice for Storage of Processed Silver-Gelatin Microfilm.

From a study of these documents, three important points emerge:

(1) Even though the standards and proposed NARS rule apply only to silver-gelatin films, the film itself is not "archival" however, it can be suitable for the preservation of records of permanent value if

(2) the film is stored under stringently specified archival conditions, and if

(3) the silver-gelatin film has been properly manufactured and processed.

The interdependence of these three points is recognized by NARS, ANSI, and everyone who has worked on the problem. There can be no archival quality without archival conditions of storage, and present standards apply to silver halide gelatin films only. Physical and chemical tests can be devised which will insure that the film has been properly processed and is suitable for archival storage. Such tests become "standards," but they do not predict how long the film will last.
To estimate the permanency of film, accelerated aging tests are devised where the film is exposed to abnormal conditions for a relatively short period of time. "Standards" are established for these conditions; but, is it valid to argue that film still stable after it has been held at 75°C and 75 percent R.H. for 3 months will also be stable for 100 years if it is held at 20°C and 40 percent R.H. during all that 100 years? One cannot really be sure until the full century has elapsed.

During accelerated aging tests, the film product is abnormally stressed far beyond what it would be in actual usage. For the data to validly predict long-term effects, it must be unequivocally shown that the observations made under abnormal stressing are due to the same phenomena that occur under conditions of actual use. Data from changes due to the abnormal stress (which would never occur under normal conditions) should not be used (e.g., melting of gelatin in silver halide films exposed to extreme heat). It should be readily apparent that no accelerated test can be viewed as valid until aging under normal conditions has been correlated with predictions made from data developed under abnormal conditions.

Development of uniform "standards of archival quality" for microfilm is further complicated by the fact that each type of film ages by a different mechanism. The same standards cannot be applied to all types. For instance, all non-silver films would easily pass the tests for residual thiosulfate required before silver halide films can be certified as archival because thiosulfate is not used in the processing of non-silver films. Obviously, the fact that non-silver films meet the thiosulfate standard by itself does not mean that they are archival.

Finally, and probably the biggest problem of all, is that "standards" infer standard conditions. There is considerable variation in the ambient conditions of libraries in various parts of the world. In addition, the equipment used and how often a particular film is used differs considerably. Very few libraries meet the standard archival storage practice specified by ANSI much less those proposed by NARS. Until some standard conditions (or range of conditions) are established for research libraries, it will be very difficult to develop meaningful quality standards.
for microfiche they procure. Since research libraries do not meet archival standards, no film they procure can be considered archival regardless if it is silver halide, diazo, or whatever.

The complexity of trying to devise accelerated tests for wear, fading, discoloration, and other effects of the aging process under widely varying conditions cannot be minimized. Therefore, the best that can be done is to devise tests which give an approximation or educated guess as to the ultimate usability of the films. Some of the variable parameters which must be considered are:

- Chemistry and physics of the imaging system
- Film base
- Incident light—strength and spectral composition
- Exposure time to incident light—continuous or intermittent
- Ambient conditions (temperature, R.H.) in use
- Ambient conditions (temperature, R.H.) in storage
- Film container
- Wear due to use and handling
- Definition of usability—at what point in the aging process is film no longer usable for reading and/or for printing.

Late in 1975, facing up to this dilemma, Dr. P. Z. Adelstein of Eastman Kodak and Chairman of ANSI PH1-3 Task Group on vesicular and diazo film, which had been established to develop standards for these films, wrote to Dr. James B. Rhoads, the Archivist of the United States, requesting clarification and guidance. Understandably, given the complexity of the problem, the reply he got is hardly a model of clarity. It wishfully points out that the term "archival" is synonymous with "permanent," and "they have the same meaning; that is, forever." The Archivist appreciated that no one could guarantee that everything now classified as archival would be kept forever. He then went on to say:

"Permanent or archival record film can be defined as any film that is equal to or better than silver film, as specified in ANSI specifications PH1.28 and PH1.41. We realize that equating other film types to silver may not be the best criteria, but at this time it is the only standard that we have. Silver has been around long enough to lend some
credence to its stability as an archival material, yet if newer materials can be qualified they too should be considered for certification.\(^{39}\)

This puts all non-silver halide films in a Catch 22 situation. Under present standards, only silver halide stored under archival conditions, designed for silver halide (and which prohibit storage with other types of film) can be certified as archival. Because of differing aging mechanisms, there is no absolutely sure accelerated aging method which will equate the potential age of non-silver with that of silver films. Therefore, under existing conditions, it will be next to impossible to certify anything but silver halide films as "archival."

Yet, as they apply to libraries, the terms "archival" and "research" are contradictory; an archive, as now defined, cannot be used as a research library where the files are actively used. The way out of the impasse appears to be some other terminology which will realistically express image and film durability for a fixed period of time under conditions found in research libraries. A distinction should be made between permanency required by archives and durability required by research libraries. This distinction already exists for paper products. According to "The Dictionary of Paper,"\(^{40}\) "The permanence of paper refers to the retention of significant use properties, particularly folding endurance and color, over prolonged periods." Durability expresses "The degree to which paper retains its original qualities under continual usage." A start in that direction has been proposed by Carl Spaulding of the Council on Library Resources in a memorandum circulated on July 7, 1978, to the Micropublishing Committee of the American Library Association entitled, "A Solution to the Impasse Over Silver/Non-Silver Microfilm." The solution he proposes is to require micropublishers to deposit archival quality, second generation masters in a special depository where it would be held inviolate as protection against any set of conditions causing a micropublisher to be unable to make additional copies available. This would be the archive in which stringent storage conditions would prevail to insure permanence. The library could then buy less expensive, more durable, non-silver film for their active files.
Studies On Microfilm Stability From The Literature

The literature on the stability of the various photo-imaging systems is fairly extensive. Many of the investigations were carried out in the laboratories of manufacturers and deal with useful film life predictions under standard conditions or compared to silver. The literature is lacking, however, on image stability under conditions of actual use. Only one reference was found in the technical literature authored by a librarian, and it dealt primarily with use of microforms in a medium-size university library. It detailed accession, retrieval methods, and student acceptance with no mention of stability.

Silver halide photography has been around longer than any of the other systems. It is now approaching the ripe age of 150 years, and some of the earliest examples are still around in our museums. Eugene Ostroff, Curator of Photography of the Smithsonian, was able to copy and actually enhance image definition of one of Talbot's prints made in 1835. Most other studies on silver deal with chemical factors affecting image permanence. Many of these findings have been incorporated in various ANSI standards to which we have previously referred. ANSI PH1.41 includes an accelerated heat test which silver films destined for archival storage must pass. It requires that the "film image shall show no degradations which would impair the film for its intended use" after the film has been incubated for 30 days at 60°C ± 2°C (140°F ± 4°F) and 70 percent ± 2 percent relative humidity. What this means in terms of storage life under "normal" or "archival" conditions no one knows.

Although diazo images have not been around 150 years, studies have been made on some that have been around as long as 30 years. In an address to the 1973 Annual Conference of the National Micrographics Association, Dr. A. H. Stuart of Bruning Division, Addressograph-Multigraph Corporation, had this to say:

"...diazo prints are also capable of retaining their utility over periods of prolonged storage. How long? We don't really know--reliable predictions of longevity are difficult. Fortunately, there is by this time considerable information from actual experience. Engineering films which have been stored in ordinary office files for more than 30 years can be verified from first-hand experience as intact and fully usable. As mentioned above, diazo microfilms were put..."
into use more than 25 years ago and prints which have been filed since 1945 to 1947 are reported to be in excellent condition.\textsuperscript{43}

It must be stressed that the "ordinary office files" were not under archival conditions, and the files were actively used.

In 1967, Dr. David P. Habib wrote:

"During the period of the last 40 years, there has been ample proof that suitably formulated diazotype prints are long lived. Several years ago the National Association of Blueprint and Diaz° Coaters embarked on a program to collect information on this subject. Diazotype manufacturers were asked to supply the oldest prints available illustrating the print aging qualities of diazo materials. These have been incorporated into a book, now in the files of the Executive Secretary of the NABDC.

"In addition, a detailed questionnaire was sent to the earliest users of diazo microfilm, namely the Social Security Administration and the Bureau of Public Debt, asking for their experience with diazo film. The reports were highly favorable, indicating that diazo film showed no signs of significant deterioration over a use period of about 20 years."\textsuperscript{44}

Numerous studies have been conducted on diazo films which employed accelerated aging techniques. In 1964, Barba & McKinney studied the action of light from a 300 watt tungsten lamp on film in a reader and on the same film exposed for 8 hours to a carbon arc in a Fadeometer. They also studied accelerated aging of the material by conditioning it at 100\textdegree C (212\textdegree F). Loss of density (both visual and printing) was measured, and varying degrees of fading were found with two diazo microfilms showing "superior resistance to fade." Much less density change was found after heat aging than with light exposure, and it was concluded "dark storage should not significantly affect azo or microfilm permanence."\textsuperscript{45}

Nelson studied image fading for periods up to 100 hours in a Fadeometer--the ultraviolet content of which is equal to that of noonday sunlight. Different rates of fade were found for different films but were generally usable up to 25 hours exposure. He also exposed film in a duplicator for 900 times for 20 seconds each
time (equivalent of 5 hours exposure). The films were still usable. He concluded that, from a practical standpoint, diazo films could withstand substantial amounts of exposure without serious loss of either readability or reproducibility.

Reporting to the 1973 Conference of NMA on a new heat developed diazo film, Dr. Joseph H. Shepard of 3M's Microfilm Division, had this to say:

"...As with any diazonium material, the image is an organic dye and it is subject to fading when exposed for prolonged periods of time to light. For example, after 3 hours of continuous exposure in the film plane of a typical engineering drawing reader-printer, the dye image of Type 788 will fade approximately 12 to 15 percent. Even after this severe test, all of the information is still legible and readable prints can be produced."

The Broadhurst Report

More recently, R. N. Broadhurst of Great Britain's National Reprographic Centre for Documentation published a report which created quite a stir among librarians. It was on an extensive investigation into the effects of light exposure on diazo microfilm. He tested 12 "representative" films with a variety of light sources in a wide range of equipment. He established, based on some subjective tests, that film which had faded to 0.5 minimum background visual density coincided with a fair or just barely readable quality category. The amount of time to reach this fade level varied considerably among the various films under the wide variety of conditions employed. In a Xenotest unit (similar to our Fadeometer), the slowest fading film took almost 53 hours to fade to 0.5 density, while the fastest took just under 20 hours.

The films were also exposed to daylight, and the rate of fade varied by a factor of 3.5. A slight increase in the minimum printing density was also observed which showed as a slight yellowing of the film.

The effects of combined indirect daylight and fluorescent ambient room lighting on film was minimal after exposure for 300 days--the worst case showing a drop of 0.11 in the maximum density. There was also a very slight darkening noted in the
D min. This test most closely approximated actual use conditions, but it is hard to believe that an unprotected microfiche would be left around for almost 1 year.

Fading was studied in a variety of readers and reader printers--24 in all. The time it took to fade the image to the 0.5 level varied by a factor of 20. For example, one diazo took 14 hours in the fastest fading reader, but 240 hours in the slowest. Obviously, the amount of fading is dependent on both the film and the reader in which it is exposed. Heat filters interposed between the light source and the film increased the time it took to fade the film by a factor of 1.5 to 3. Not surprisingly, they were able to draw the general conclusions that with low lamp wattage and magnification, fading is relatively low compared to those reader printers with high lamp wattage and magnification.

It is difficult to draw general conclusions from such an exhaustive investigation. Some of the worst cases and combinations of film and readers warrant apprehension. On the other hand, they proved that the films tested will stand a significant amount of fading before their usefulness is seriously impaired. The fact is that the amount of energy, both as heat and light, required to reach the 0.5 density level is considerable under the accelerated test conditions. No attempt was made to relate this to expected shelf life under archival conditions, and only generally to actual conditions of use where it takes a long time to reach the total energy required to match results obtained under accelerated conditions.

**Predicting Image Stability By Chemical Kinetics**

It has been pointed out previously that estimates of performance under archival conditions based on data obtained under accelerated aging are only valid if they can be correlated with data observed under normal conditions. However, the changes observed as microfilm ages are chemical in nature. The rate of aging can be considered a problem in chemical kinetics. The rate of a chemical reaction depends upon concentration of reactants, temperature, radiation (e.g., light), and the presence of a catalyst or inhibitor. As the temperature increases, so does the rate of the reaction, within certain limits. In elementary chemistry one learns that for simple reactions, the rate approximately doubles for each 10°C increase.
The actual rate of a reaction for each temperature is obtained by relating the total chemical change with the time it took for it to occur.

The most satisfactory method for expressing the influence of temperature on reaction velocity is the use of an equation first proposed by S. Arrhenius in 1889. If specified changes with time are observed at two or more elevated temperatures, some function can be obtained from which the time it will take for the same changes to occur at normal temperatures can be extrapolated. One can then use the demonstrated effect of temperature on rate of reaction according to the Arrhenius equation. In the classical use of this equation, it is necessary to obtain the specific rate of reaction for each temperature. However, it is possible to use changes in some property if the specific reaction is not known. This is done by observing changes at selected elevated temperatures and plotting them against time, obtaining a rate constant. Normally, the plot of a chemical reaction is a straight line when the logarithm of the rate constant is plotted against the reciprocal of the absolute temperature. (The absolute temperature is centigrade temperature plus 273, and is expressed as °Kelvin.) From this data, the high temperature results can be extrapolated to room temperature. However, it must be shown that the rates of change being followed adhere to the same rate law expression at each temperature studied to insure that a completely different chemical reaction is not being ignored which may be taking place at the higher temperature. For this, the plots for each temperature should be parallel.

This method was used by Browning and Wink to study deterioration of paper. Changes in certain properties of paper, such as folding endurance and tensile strength, which were known to occur during normal aging of paper, were studied at elevated temperatures. The paper was placed in sealed glass tubes in order to avoid factors such as relative humidity from distorting the data. Following the customary application of the Arrhenius equation to the data obtained, they were able to predict, at least in principle, paper permanence at normal temperatures.

The method was applied to dry silver film stability by Kurtilla. The data used was taken from aging tests of 3M's Type EBR (Electron Beam Recording) film at high levels of temperature and relative humidity. He monitored the change in D min. at different times to establish how long it would take for the film to reach a
previously set "failure" condition at the abnormal conditions. In one set of tests, the film was considered unusable when the Dmin. reached a density of 0.20 from an initial Dmin. of 0.08. Plots were generated from the results from which predicted aging at lower temperature storage was extrapolated. The predicted life expectancy for the EBR film was 25 years, and correlates well with data obtained under actual conditions over an 8 to 10 year period.

The Arrhenius equation was used by O. J. Cope to study aging of vesicular films. First, he demonstrated experimentally that the thermal stability of vesicular images is related to the effective glass transition temperature (Tg) of the vesiculated polymer matrix. Tg is defined as the temperature at which an amorphous material changes from a brittle, glass like state to a plastic state. The boundaries of a vesicle are composed of the polymer in the vitreous state. As it is heated and becomes plastic, the vesicles collapse and the image is lost. Obviously, at temperatures above Tg changes occur in density which are caused by a different mechanism than the one which causes density changes below this temperature. Under normal conditions, the film would never be exposed to such high temperatures. Thermal aging data below Tg was used to predict room temperature stability over long periods of time by submitting such data to the Arrhenius equation; the density loss rates found were so low that the image stability was equivalent to "many thousands of years."

Adelstein and McCrea studied the application of the Arrhenius equation to diazo films as part of the investigation of the ANSI Task Group to which we have previously referred. (It is interesting to note that both Kurtilla's firm, 3M, and Cope's firm, Xidex, are represented on the ANSI Task Group. The image changes in diazo films with aging, particularly in the dark, are much more complex and not fully understood; so, they had a tougher problem in application of the Arrhenius relationship than did Kurtilla and Cope.

As a result of their work, Adelstein and McCrea developed an accelerated age test for "long term" and "medium term" film representing film with a useful life of 100 years and 10 years respectively. They postulated that the usability requirement of diazo film is no longer met if either:
The density difference between the low (0.1) and high (1.2) density decreases to a value less than 0.8, or

(b) the density of the low density patch (0.1) exceeds a value of 0.4.

The criteria apply to both visual and printing density; thus, the film must pass four tests.

To be classified as "long term," the film must not fail any of the four criteria after incubation at 80°C (176°F) for 50 days. For the "medium term" classification, the film is incubated for 14 days at 70°C (158°F). These designations and tests have been proposed as ANSI Standard PH 1.60 for "the stability of ammonia processed diazo photographic film." The proposal is being balloted, and Dr. Adelstein has told us that he expects approval of it in the very near future.

The Adelstein paper, together with the Broadhurst report, have caused a great deal of concern in the library community; and they have been cited as scientific evidence that the GPO decision to furnish statutory libraries with third generation diazo microfiche should be reconsidered. In part, the concern exists because the ANSI working group included "archival film" (as defined by the Archivist) as a third type of film classification; and none of the diazo films met the archival criteria.

Five diazo films and a silver halide film were used in the Adelstein tests. There were insufficient density changes in the silver halide film in any of the four image criteria used to estimate a "useful life"; whereas, at least one of the four possible criteria could be used for each of the diazo films. The tests are continuing; but, at 1,000 days out, Adelstein was able to extrapolate useful life predictions at normal temperatures on only 9 of the 20 possible. These ranged from 9 years to 350 years. Six of the nine data points were based on the not less than $\Delta D 0.8$ criteria--three in the visual, and three in the printing density. Three were based on the change in $D_{\text{min}}$ to 0.4, all on visual density. Interestingly, the film with the shortest predicted useful life failed in only one of the four criteria; and that one was the decrease in printing $\Delta D$; this film also showed base degradation.
The proposed standard may have some merit and may be useful, particularly since there is nothing better around. However, the "useful" life predictions developed are not very convincing. Apart from the paucity of data reported, the "usability" definition listed in the paper is, in our opinion, a serious misrepresentation, particularly since (quoting from the Adelstein paper): "The Task Group took the position that usability applies only to commonly used standard photographic or viewing techniques and does not cover unusual reproduction approaches." The fact is that $\Delta D$ can drop to 0.5, and the film can still be read and printed in routinely used equipment. This was established in the Broadhurst report and corroborated in tests made at GPO. The increase in $D_{\min}$ to 0.4 has not been reported anywhere under normal use conditions.

If the Task Force had not pinned their usability definition to the criteria they established, there would be no quarrel with their use of the values as preset points in an Arrhenius type investigation. However, the fading mechanism of diazos is complex; and at different temperatures, different reactions can take place. Adelstein finds the similarity of density changes among the film tested as "fortuitous." He even admits to the possible existence of diazo materials whose fade rate is not temperature dependent.

Consequently, and based on the evidence presented, his conclusions regarding useful life predictions have to be considered shaky, at best.

As Dr. E. W. Bennett of Scott Graphics put it in a private communication:

"He simply doesn't show the curves for each characteristic at all temperatures and derive a linear transform to get a figure analogous to a specific rate constant. Surely one cannot equate the time required to exceed the specific limit $\Delta D/t$ to the equivalent of a rate constant when the curves used to get the figures are anything but linear. In addition, when D-max is dropping and D-min increasing any measure of the $\Delta D$ with time is a product of two rate expressions and not even as likely as one overall expression for just one density level's behavior to be adequately described by Arrhenius behavior."
Still, the application of the Arrhenius equation is a promising method for predicting image stability under normal conditions if one limits it to one type of chemical mechanism and heeds the admonition in the Browning and Wink work on paper aging. Quoting from their paper:

"Thus, the ideal case is one in which rate plots are all linear and the Arrhenius plots are all linear and parallel. It would then become possible, from the results of a single period of accelerated aging at a chosen elevated temperature, to calculate the value of a selected property after any specified time at ordinary temperature."

It is not wrong to try the approach to such a complex system as diazo image stability; but the application should be rigorous so that apparent conformity is, in fact, going to afford valid predictions.

**Testing At GPO**

Read in the proper perspective, the literature review is encouraging despite the misgivings of many librarians. Excluding "Worst case" results reported and refusing to fall into the "equal to silver halide" trap, it appears that the decision to furnish diazo fiche was a sound one. Nonetheless, in view of GPO's responsibilities and the legitimate concerns of the library community, it was decided to submit the actual microfiche we furnish to a variety of tests, many of which are still continuing. The objectives of the tests are:

- To assure ourselves and the librarians that we were not supplying an inferior product.

- To develop durability quality attributes for microfiche (based on accelerated testing) to use in future procurements. This is in conjunction with GPO's Quality Assurance through Attributes Program.

- To establish durability predictions under conditions existing in depository libraries.
To develop data from which recommendations for reasonable storage and use could be made. Broadhurst has a sensible suggestion:

"It might be useful to users if some form of standard index could be developed which would indicate the resistance to loss of contrast of diazo materials and the fading rates of microform equipment covering readers, reader-printers, production printer, and duplicators."

The GPO investigation is on going and may not be completed for a year. Production line fiche, as furnished to libraries, are used in the testing. Presently, the Government Printing Office contractor has the choice of furnishing either black, medium low contrast fiche as a 5 mil polyester base or a blue, medium high contrast fiche on 4 mil polyester base. Both have been tested on a preliminary basis following suggestions found in the literature. Some new tests were devised which we hope to submit eventually for publication. The GPO furnished fiche score well; both types meet the "long term" requirements of the proposed ANSI Standard PH 1.60 (100 years or more). They rank with the best of the fiche reported by Broadhurst in fadeometer testing, and exposure to ambient light.

We believe we now have experimental evidence that the resistance to wear under actual use conditions of the diazo is superior to that of silver halide. This had been claimed in the literature but only based on a priori reasoning without experimental data. The claim had been disputed by some librarians. In our tests, the film is abraded in a Sutherland rub tester using "crash lining" as the abrasive material. This is the stiff fabric material glued on the backbones of books before they are covered. The films were rubbed for 500 strokes with a 6 pound weight under ambient and at slightly elevated temperatures. The image wear is determined as percent loss by reading the films before and after testing in a Bausch & Lomb Image Analyser. The results are tabulated below.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Black Diazo</th>
<th>Blue Diazo</th>
<th>Silver Halide</th>
</tr>
</thead>
<tbody>
<tr>
<td>23° (73° F)</td>
<td>12</td>
<td>12</td>
<td>33</td>
</tr>
<tr>
<td>38° (90° F)</td>
<td>7</td>
<td>7</td>
<td>70</td>
</tr>
</tbody>
</table>

\[ \text{Average Percent Loss} \]
Obviously, the resin binder in the diazo fiche is either a thermoset polymer or loses plasticizer and becomes harder at elevated temperatures; whereas, the gelatin on the silver halide fiche begins to soften.

As is apparent, the difference in resistance to rub (as measured by image loss) is significant. We are now trying to relate the test to wear actually occurring in libraries. This is an example of a quality attribute which at GPO we define as "definable and measurable characteristics which affect the excellence of the end product."

Such quality attributes are essential in any quality assurance program aimed at bringing costs into line with demonstrated needs. Cost effectiveness can be quantified, simplifying the problem of assuring that the specified needs of the products are met at the least cost.

Conclusions

- Under archival conditions, as presently defined, diazo fiche may not have the same degree of permanence as silver halide; but they will be usable for at least a hundred years or more.

- Under conditions which actually exist in research libraries, both diazo and vesicular films are superior in resistance to wear and to biological attack.

- The diazo microfiche GPO furnishes depository libraries is adequate for their needs.

We do not see any set of conditions occurring which will render the fiche completely unusable. In the unlikely event that this should occur, provisions have been made to replace the fiche. The replacement would be free if the failure resulted from poor quality, just as we would replace a book if it was defective. In case the fiche failed because of conditions in the library, it would be replaced at a price to include direct and indirect cost, just as we would replace a book which had worn out or was vandalized.
In summary, GPO has undertaken a considerable effort in its Quality Assurance through Attributes Program aimed at fulfilling its responsibilities to the libraries and the public. The effort applies equally to microfiche as it does to printed products.

Acknowledgments

During the preparation of this technical review, the author had a great deal of assistance in the form of advice from many sources. George Hodgins, E. W. Bennett, and F. E. Dailey, Jr., of Scott Graphics sent information on their TEP system and unpublished reports on updatable microfilm and dark stability predictions. O. S. Cope of Xidex was kind enough to send an advance copy of his paper on vesicular film stability; 3M's W. J. McGlone, Jr., sent data on the Ovonics film, and P. R. Shaw did the same on their dry silver technology. Carl Spalding of the Council of Library Resources made several valuable suggestions. Many others were kind enough to contribute their time and knowledge.

Without the encouragement of Carl A. LaBarre, Assistant Public Printer (Superintendent of Documents), and John Livsey, Director of the Library and Statutory Distribution Service, the report might never have been completed.

Finally, the help from the staff of the Quality Control and Technical Department must be acknowledged, and, in particular, the assistance of Paul J. Giannini, who supervised much of the testing, and Laura Mell, a summer intern with the department who made many of the readings.

My heartfelt thanks are extended to all of them.
REFERENCES


3. ANSI PH1.28-1976, Specifications for Photographic Film for Archival Records, Silver Gelatin Type on Cellulose Ester Base.

4. ANSI PH1.41-1973, Specifications for Photographic Film for Archival Records, Silver Gelatin Type on Polyester Base.


34. HAMILTON, J. F., *Chap. 7 in Theory of the Photographic Process* (see Reference 5, above).


48. BROADHURST, R. N., An Investigation of the Effects of Exposure to Light on Diazo Microfilm, NRC Publication No. 5, July 1976. (Address inquiries to National Reprographic Centre for documentation, The Hatfield Polytechnic, Endymon Road Annexe, Hatfield, Hertfordshire, AL 10 8AU, Great Britain.


