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# The Acetate Negative Survey

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## THE ACETATE NEGATIVE SURVEY

# FINAL REPORT A PROJECT FUNDED BY THE UNIVERSITY OF LOUISVILLE AND THE NATIONAL MUSEUM ACT

David G. Horvath University of Louisville Ekstrom Library Photographic Archives February 1987

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# THE ACETATE NEGATIVE SURVEY FINAL REPORT

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#### INTRODUCTION

Beginning in the early 1970s curators, librarians, and archivists in charge of collections containing historical photographic negatives began to notice that certain portions of their collections were beginning to display serious deterioration. The damage observed typically included badly distorted negatives showing severe shrinkage. Also, because of the base shrinkage, the various layers of the film laminate were becoming separated, making the negative unprintable. The smell of acetic acid accompanied this phenomenon.

Because these negatives had been manufactured relatively recently, it was obvious that these negatives were not on cellulose nitrate base and that they were in fact "safety" negatives. At this point in the discovery of the problem, most of the affected negatives seemed to date from the late 1940s and early 1950s. Some of the early evaluations of the problem considered these negatives to be isolated examples of degraded cellulose diacetate film base which had become unstable due to extreme temperature and humidity conditions.

Since that time, more historical negative files have found their way into various repositories. Many of these collections suffer similar problems and the total number of degraded negatives is increasing. The once small "pockets" of degraded negatives are getting larger, and the dates of origin are no longer limited to a few years. Many collections with safety negatives dating from 1925-1955 are finding these problems in their files.

To make matters worse, very little information about these negatives is available to these caretakers in the literature with which they are familiar. What little mention there is in curatorial or preservation sources is essentially accurate in that it stresses the need for the isolation and duplication of what have been called "diacetate negatives." But these sources lack consistency in terminology, a reasonable explanation of the problem, or a true idea of its scope. Much of this information is simply not available. The film manufacturers, who genuinely had not been aware that the situation had become so widespread, responded that the problem is chemical degradation of the film base due, primarily, to improper storage. Although accurate, this seems to place the blame on mismanagement by the repositories themselves.

At the same time, exaggerated stories about the situation are being traded between anxious curators and a folklore about these negatives is beginning to emerge. It is the purpose of this project to

begin the process of defining the problem in such a way that a firm groundwork will be laid for future work. While much of the tone of this report and its recommendations will be directed towards those who work directly with these collections, it is hoped that it will be also useful for those who will continue the technical work that still needs to be done to more fully understand the problem. This report combines a distillation of the existing technical knowledge and practical observation. It represents a very conscious effort to state accurately what we know, what we do not know, and what we can reasonably do about the present situation.

This project was funded by the University of Louisville and the National Museum Act. Its objectives are the following:

- 1. To survey existing negative collections which can be accurately dated from 1925-1955, which contain a variety of manufacturers' film and film types. These negative collections represent material used in various photographic applications including the newspaper, commercial, scientific, and fine arts fields. Among other things, the survey will define the scope and extent of the problem throughout the country and will determine the correlation, if any, between dates, notch codes (film types), and film base deterioration.
- 2. To obtain information from interviews with those who are/were involved in the research, manufacture, and testing of these negatives.
- 3. To make recommendations for the preservation of these negative collections and other collection management considerations.
- 4. To provide a bibliography of film base history, manufacture, and deterioration.

#### **SECTION 1 - HISTORY AND CHRONOLOGY**

In 1929 a fire at the Cleveland Clinic, a large hospital in Cleveland, Ohio, dramatically escalated the efforts of manufacturers of photographic materials to replace cellulose nitrate film base. The deaths that resulted from the inhalation of poisonous smoke released by burning x-ray negatives on cellulose nitrate base created a new drive and impetus for the manufacture of a film base which would not burn as violently and rapidly as cellulose nitrate. The technological challenge was to manufacture a material which would also duplicate some of the very desirable features of the nitrate, such as its resistance to moisture and its outstanding mechanical strength and dimensional stability. The difficulty in perfecting such a material is indicated by the fact that certain film products, most notably, professional motion picture film, continued to be made on cellulose nitrate film base until about 1950.

Cellulose acetates were first used during World War I to coat the fabric wings of aircraft but were not used as a film base until 1923 when 16mm amateur motion picture film was manufactured using cellulose acetate.[1] Cellulose acetate is manufactured by combining cotton linters or wood pulp (the sources of the cellulose fibers) with acetic acid, acetic anhydride, and a catalyst such as sulfuric acid. The esterification process substituted acetyl groups for the hydroxyl groups on each glucose unit of the cellulose molecule. "Fully esterified" cellulose has all three of its hydroxyl groups substituted, producing cellulose triacetate. A partially hydrolyzed acetate contains about 2 1/2 acetyl groups per glucose unit and this material is called cellulose diacetate. It was used commercially long before cellulose triacetate because it was soluble in available and less expensive solvents.

In about 1925 Kodak was the first manufacturer to introduce sheet film on a "safety" film base. Agfa, Defender, Dupont Defender, and Hammer began manufacturing safety film on supports made from cellulose diacetate somewhat later, in the mid 1930s. Both Agfa/Ansco and Defender continued to use diacetate until they switched to polyester in 1955.

Cellulose diacetate was not the ideal film base. It was less resistant to moisture than cellulose nitrate and also inferior in other physical properties. Its affinity for moisture increased the possibility for physical distortion due to humidity. Older cellulose diacetate films are often found to have some degree of distortion. Also, coating speeds in the manufacture of this product were slow and it was expensive to manufacture. Therefore, Kodak did not manufacture diacetate film base after about 1940 when other esters of cellulose were introduced.[2]

During this period Kodak set up a special research laboratory to experiment with the esterification process in the hope that they could come up with a more optimal film base. This project was headed by H. Clarke and Carl Malm who concentrated on combinations of mixed acid esters of cellulose. In 1927 they produced the first of these mixed esters, cellulose acetate propionate. This was considered a major accomplishment for the film industry and it led to continued work with the mixed cellulose esters, including the very useful cellulose acetate butyrate introduced in 1936.[3] Soon Kodak began to manufacture the mixed cellulose esters at its plant in Kingsport, Tennessee. These products became a major base material manufactured by Kodak in the 1940s although cellulose nitrate was still made in large quantities.[4]

Cellulose esters vary in their physical and chemical properties, such as melting point, specific gravity, moisture absorption, and solubility in plasticizers and solvents, depending on the degree of esterification of the hydroxyl group in each glucose unit and the ratio of acetyl to propionyl or butyryl.[5] Film bases of mixed cellulose esters represented a real improvement over cellulose diacetate in terms of their dimensional stability and certain other physical characteristics. Cellulose acetate propionate was widely used for amateur films in the 1930s and 40s and cellulose acetate butyrate was used for x-ray and professional sheet film. 35mm professional motion picture film requires considerable toughness and dimensional stability and it continued to be manufactured on cellulose nitrate until the introduction of cellulose triacetate.[6] Cellulose acetate butyrate is still used for some professional film applications.

The need for a satisfactory support for professional motion picture film was the driving force behind the experimental work which led to the development of a "high acetyl" film base, now known as triacetate. Cellulose acetate propionate and butyrate, while superior to cellulose diacetate, did not have the strength for sufficient wearing qualities and it was not rigid enough for steady projection under hot, high intensity bulbs. Cellulose triacetate, the product of complete acetylation of cellulose is very difficult to dissolve in common solvents and the resulting film product is brittle. Research indicated that an in-between chemical composition with slightly less than three hydroxyl groups substituted by acetyl groups resulted in a film with the desired qualities.[7] Also, after World War II methylene chloride, the coating solvent used for this formulation, became available in commercial quantities at a reasonable price. Cellulose nitrate was then effectively replaced with this triacetate material and nitrate

production stopped in the United States in 1951.[8] Most professional motion picture film is still made from cellulose triacetate.

Although the introduction of triacetate or high acetyl cellulose solved many of the problems relating to motion picture film base, there were still several applications for which a more dimensionally stable material had to be found. All cellulose derivatives have an attraction for water molecules which cause some degree of dimensional change. For aerial mapping applications, engineering drawings, and color registration in the graphic arts industry, extreme dimensional stability is required.

Several plastic materials were used for such applications with limited success after 1945. Polyvinyl chloride was used for a time for graphic arts films from 1945-1955. Polystyrene, which enjoys wide application for molded articles, was used for film after 1954 and was widely accepted in the graphic arts industry.

But it was not until the introduction of the polyester, polyethylene terephthalate, that a plastic film base found acceptance for nearly all photographic applications in which dimensional stability was of prime importance. A polyethylene terephthalate film base called "Cronar" was first produced by the Dupont Company in 1955 and later was manufactured by Kodak and known as "Estar". A non-photographic grade of the material called "Mylar" is available from Dupont.[9]

In 1957 Agfa/Ansco introduced a film made from another polyester called bisphenol-A polycarbonate. It was extremely resistant to moisture and dimensionally stable, making it desirable for graphic arts and aerial applications. It could be manufactured with solvent casting, like the acetates, which eliminated the need to add the expensive melt casting equipment needed for polyethylene terephthalate production. But the film was still expensive to manufacture and did not possess the other desirable specifications found in polyethylene terephthalate film, so the product did not find wide acceptance.[10]

A summary of currently used photographic film bases is given in the following table:

# **CURRENT FILM BASE USES [11]**

Application	Film Base	Reason
Graphic Arts	Polyester	dimensional stability
Aerial and		
Industrial		
Uses	Polyester	dimensional stability and
		mechanical strength
X-Ray	Polyester	greater stiffness of polyester
		when wet
Microfilm	Triacetate	solvent splicing
	Polyester	thinner, better long-term
		storage characteristics
Professional		
Sheet Film	Polyester	greater strength, flatness
	Cellulose	for compositional layout where
	acetate	cutting or dissolving film
	butyrate	base is required
Professional	Triacetate	solvent splicing
Movie Film		
	Polyester	strength and dimensional
		stability
Amateur Movie		
Film	Triacetate	core set* properties, solvent
		splicing
Amateur Roll		
Film	Triacetate	core set* properties

<sup>\*</sup>core set refers to the tendency of a film base to conform to the diameter of the core after winding or storage. With acetate negatives this core set is lost during the wet processing stages and the resulting negatives or slides are flat.

#### **SECTION 2 - MANUFACTURE OF ACETATE FILM BASE**

This report will deal only with the solvent casting method of making cellulose acetate bases and not with the melt casting of polyester film base. Several articles listed in the references give very good, detailed descriptions of these processes.[12]

All cellulose ester base is manufactured using the solvent casting method. This involves dissolving the polymer, which is in the form of pellets or flakes after the initial esterification process, in a suitable solvent or usually, in a group of solvents. Plasticizers are added to the mixture to improve the product's moisture resistance and decrease its burning rate. Triphenyl phosphate is often the plasticizer of choice for acetate films and it is used, depending on the application of the product, in quantities from 5 - 25% by weight of the cellulose ester.[13]

The resulting mixture, or "dope" has the consistency of honey. This solution is cast by spreading on a heated drum or belt at a speed slow enough for the base to be stripped as solvent evaporation occurs and the base attains sufficient strength. The "green" support is then passed through a series of heated chambers to remove additional residual solvents. At this point special coatings and adhesive layers are applied. The solvent evaporation or curing continues until the base is rolled in its final form.

Presently Kodak makes its dope continuously. All ingredients including solvent mixtures, plasticizers, and acetate ester are measured and controlled automatically. The metering speed of the ingredients is automatically keyed to the dope demand and process specifications and the temperature of each stage of the process is accurately controlled. Before about 1960, Kodak made all of its dope in batches where a fixed quantity of material would be produced from a specified mixture of ingredients.

The industry has thoroughly studied the effects of different solvent and plasticizer combinations on both the physical properties of the resulting base and the speed at which it can be manufactured. Increasing coating speeds while retaining product quality is a high priority. Various combinations of solvents and plasticizers have been used for each product's specifications.

For certain products, a higher speed method has often been used during the casting operation. This involves the gelation or coagulation stripping method which allows the base to be stripped off the heated drum while still quite "green." This method basically uses a combination good solvent/poor solvent mixture and the former is evaporated.[14]

The evaporative stripping method which, allows more of the solvents to evaporate before the base is stripped, has been used to meet the extremely critical specifications required for motion picture camera negative film.

The curing of the base is also very important for the properties of the final product. The speed of the curing process is determined by the specifications for the product being produced and is affected by the plasticizer and solvent formulations. Modern film manufacturing has all but eliminated the possibility of error in this complex process. Ingredients are premeasured and metered by computer controls. Temperatures in all areas of the casting machine are automatically recorded and continually checked. As described by Dennis Sheffield in his excellent article about triacetate film manufacturing in England: "By ringing the changes on all the factors which affect the character of the base, the manufacturers are able to give it desired qualities within wide limits. The processing requirements are known (or are decided in the laboratory), the machine settings are issued, and the operator's job is to see that they are maintained."[15]

#### **Surface Coatings Applied to Base**

After the base is formed and comes off the revolving drum or band, other layers are then added to the film base to prepare it for the final coating with the sensitized gelatin emulsion. These layers include some or all of the following:

- 1. **The Subbing** An adhesive layer is necessary to adhere the gelatin emulsion to the film base. In cellulose ester this may consist of a mixture of gelatin, cellulose nitrate, or acetate which is dissolved in a mixture of water and organic solvents. The water and solvents evaporate during drying providing a coating that adheres both to the acetate base and the gelatin emulsion. (Note: The effect on the stability of the film product of this nitrate layer, which is so thin as to be almost negligible, has been questioned. Extensive testing by Kodak has proven that it has no effect on either the chemical or physical stability of their own film base.)
- 2. **Anti-halation Layer** Films are often protected from halation by a dyed backing layer which absorbs light but which is decolorized during processing of the film. In Agfa/Ansco products, a blue anti-halation dye which was converted to a luco base during processing was used. It is generally colorless but is turned blue again by the action of mold or acids. Many degraded Agfa/Ansco negatives exhibit this distinctive blue color.
- 3. **Other coatings** Other surface coatings can include those intended to provide static protection by preventing surface-to-surface contact which can result in static generation, or by changing the charging characteristics.[16]

After the base is coated and dried, quality control checks are made on completed rolls to assure adherence to specifications. The rolled base stock is then delivered to the facility where the emulsion and anti-curl layers are added.

#### SECTION 3 - THE STABILITY OF CELLULOSE ESTER FILM BASE

#### **TECHNICAL LITERATURE**

Much of the technical literature discussing the stability of the cellulose esters coincides with three major technological changes in film base production. These were the transition from cellulose nitrate to the early "safety" bases, the changes which came as the superior products of high acetyl acetates (triacetate), and finally when polyester bases were introduced. Most of this literature about these products and processes relates directly to motion picture film, safety aerial film, or other film application requiring a high degree of dimensional and physical stability.

The difficult task at hand for photographic base chemists during the period 1925-1950 was to develop a base material that would replace cellulose nitrate but would duplicate some of its more desirable qualities, such as resistance to moisture and its good mechanical properties. Very little was written during the first decade after safety film was used for sheet film since it was well-known that this acetone soluble cellulose diacetate was inferior in many of its physical properties, most notably, its tendency towards high shrinkage.

Improvements in film base formulations came in the late 1930s as Kodak began to introduce the mixed cellulose esters. Most of these formulations, including the cellulose acetate butyrates and propionates seemed quite adequate for most sheet and amateur film requirements but they were still somewhat inferior to nitrate film for the all-important motion picture industry. In 1944 an important article on safety film stability by Dr. J. M. Calhoun, a well-respected Kodak scientist, introduced many concepts and facts relating to the physical stability of cellulose acetate motion picture film. He carefully examined recent improvements in film base as well as presenting some of its deficiencies for motion picture applications. The areas most thoroughly discussed were the manufacture of film base as it influences various physical properties, the effects of moisture on film, the mechanical properties of film, and a description of both temporary and permanent film shrinkage of various types. It is interesting that Calhoun concluded that "the importance of proper protection of

film against moisture changes during storage, and the exercise of a certain amount of control over relative humidity ...cannot be overemphasized."[17]

In 1947 Calhoun presented a paper at the 13th Annual Meeting of the Society of
Photogrammetric Engineers which expanded his earlier work as it applied to aerial film. "The Physical
Properties and Dimensional Stability of Safety Aerographic Film" remains the most thorough and
complete description of safety film as it was manufactured by Kodak for use in aerial photography for
topographic mapping. In this article Calhoun carefully pointed out that Kodak safety aerial film "has
never been made from, and should not be confused with, regular acetone-soluble cellulose acetate
(diacetate)." Only cellulose acetate butyrates and propionates and high acetyl cellulose acetates
(triacetates) have been used for aerial film. Calhoun cites the "continual improvements" in these products
resulting in film with superior physical properties and dimensional stability, but still admitting that
nitrate base had some advantages over safety film in certain mechanical properties.[18]

His conclusion was that by that point in time, the aerial film product manufactured by Kodak was as perfect as the nature of the materials themselves would allow. He stated that "in the final analysis film base is a plastic and the very word 'plastic' means that a material of this type will flow under stress. It cannot be expected to compare with metal or glass in dimensional stability. That is one price we must pay for the many advantages of simultaneous flexibility and transparency."[19]

The introduction of high acetyl acetate (triacetate) base in the late 1940s finally offered the motion picture industry an acceptable alternative to the cellulose nitrate base, which was still being used for 35mm motion picture film. The literature reflects the industry's excitement over this development. Dr. Charles Fordyce's article "Improved Safety Motion Picture Film Support" described the new material as the long-awaited improvement needed by the motion picture film industry. The base had the required mechanical strength for stressful projection and compared favorably to that of cellulose nitrate. In addition, the film enjoyed relatively low shrinkage characteristics.[20]

In 1960, Calhoun again reviewed the newest technology in film bases, this time the development of the synthetic polymers. Polyethylene terepthalate introduced in 1955, offered superior dimensional stability for various applications including graphic arts, aerial, industrial, and some microfilm uses. Calhoun notes that to achieve the desired high standards in dimensional stability, as related to moisture resistance and aging, a "new film base would certainly have to come from some type of synthetic polymer, that is, an organic molecule of high molecular weight."[21]

More recently, Dr. Peter Adelstein, another scientist from Eastman Kodak, has taken responsibility for the summary and synthesis of technical information about photographic film bases. His work with the photographic science community has contributed greatly to our understanding of these materials. In addition, Dr. Adelstein has worked closely with archives and museum personnel to improve the ways in which photographic materials are manufactured, tested, and stored. The words "archival permanence" have taken on a much more practical and immediate meaning in our efforts towards preservation of important photographic records and Dr. Adelstein has helped those efforts through his work with the Society of Photographic Scientists and Engineers and the development of many of the ANSI standards relating to the manufacture and storage of photographic materials.[22]

In his most important works related to this subject, Adelstein synthesizes previous technical works and his own research on the subject of photographic film bases. Adelstein wrote "The Manufacture and Physical Properties of Film Paper and Plates" in Neblette's Handbook of Photography and Reprography. [23] In this review, Adelstein (with G. G. Gray and J. M. Burnham) thoroughly discusses photographic film and paper bases in terms of raw materials, manufacture, physical and mechanical properties, and the effects of temperature, humidity and aging on dimensional stability. This work was derived from an earlier article by the same authors for the Society for Photographic Science and Engineering, "Physical Properties of Photographic Materials." [24])

The literature relating to cellulose acetate film also contains articles discussing other more specific aspects of the film base including manufacturing considerations and the determination of

physical properties for film base.[25] Various chemical choices, such as plasticizer or solvent mixtures, are discussed in the literature as well as the effects of certain environmental factors, such as humidity, and the approximate storage of cellulose nitrate negatives. Many articles analyze the shrinkage of cellulose ester film and various methods for measuring that shrinkage.

But the technical literature contains no specific mention of cellulose acetate sheet film of the kinds used for most commercial, portrait, or other non-technical applications. There are no comparable studies for these film types as there are for aerial, motion picture, and graphic arts films.

The most common type of deterioration referred to in the scientific literature is usually discussed under the broad heading of "dimensional stability." Much of this literature discusses the shrinkage of acetate films since it was recognized that they shrink as a result of exposure to air and to the various substances used in chemical development. The shrinkage was more of a problem with acetate film than for nitrate base which was in fact the reason for the continued use of nitrate film for motion picture and other technical applications.[26]

Calhoun classified the dimensional changes which occur in film according to changes in temperature, humidity, age, and processing. He distinguished between two types of dimensional change which occur: temporary or reversible and permanent or irreversible. Reversible dimensional changes come mainly from the contraction and expansion of the film due to changes in temperature and humidity. Irreversible dimensional changes come from the processing of the film and the aging process. [27] Cellulose ester films usually show a small degree of permanent shrinkage due to the evaporation of residual solvents during the photographic processing. The loss of residual solvents will cause shrinkage during the aging of the film to a degree dependent on the "amount and type of solvents remaining in the support." [28] This type of solvent loss is greater at elevated temperatures.

The literature assures us that the residual solvent content for films with technical applications is "so low as to be virtually negligible."[29] Adelstein cites limits on the dimensional change from processing for motion picture and aerial films at 0.05%. Permanent decreases in dimension with age due

to the loss of residual solvents is less than 0.5% for motion picture films and less than 0.1% for aerial films.[30] No figures are specified for other film types.

But these discussions of "dimensional stability" refer basically to a type of shrinkage or other deformation (edge curl or "solvent warp") that is generally considered minor and well within acceptable limits for all film types. The subject of this report concerns a much more serious form of degradation. We are observing serious chemical degradation and/or depolymerization of the film base of many negatives dating from 1930-1955. This degradation is different from the type described in the technical literature and is not the "normal" shrinkage or deformation caused by a minor loss of solvent or plasticizer.

#### THE DEGRADATION OF CELLULOSE ACETATE FILM

As stated, there is little discussion of this type of chemical degradation in the technical literature. "Aging" is usually described in the most general terms. The film products tested in the various technical studies were selected and produced with consistent specifications and the test conditions for various physical, chemical, and mechanical properties are well documented. What we are dealing with here are historical materials, produced by a variety of manufacturers, whose exact original composition cannot presently be verified or analyzed and which are "naturally" aged in a variety of conditions and environments, some of them extreme. What we know is that the condition of certain negatives is deteriorating rapidly.

As described, in the 1970s examples of severely degraded negatives began to show up in collections around the country. The analysis of the problem, and the opinion accepted by many until the present study, was described simply as the shrinkage of early cellulose diacetate film base. We are now beginning to arrive at a more accurate description of the situation and realize that all cellulose esters are susceptible to chemical degradation.

In 1978 Dr. Adelstein, in an article addressing the preservation of microfilm, stated the following about the problem:

"It is one of the facts of life that plastic materials degrade with time. This must be recognized and must be lived with." He continued by pointing out that some cellulose acetate negatives show more serious signs of degradation than simple shrinkage: "...life in the real world has produced examples of this film being stored in hot and humid climates without the benefit of air conditioned storage. Under such non-recommended conditions, the cellulose acetate type base degrades, becomes sticky and distorts. Eventually there is a separation of the emulsion layer from the base and the film is useless. Polyester base is more resistant to degradation under prolonged high humidity although it too will eventually degrade."[31]

No polymer chemist would be surprised by the statement that all cellulose esters degrade over time. The main question is why some acetate negatives degrade so rapidly and destructively. It will be useful to discuss a few general aspects of cellulose acetate chemistry which bear on the issue of degradation.

Cellulose plastics, unlike completely synthetic plastics such as polyester, are based on derivatives of naturally occurring high polymer "cellulose:" Vivian Stannett states that "the concern of the chemist in this field is to modify the structure of the cellulose molecule, without causing any excessive degradation. In other words, he is concerned with preventing the depolymerization of his material, and not bringing about its polymerization."[32] This task is extremely challenging considering the number of molecular substitutions, additives, and stabilizers needed to produce a clear and flexible plastic coupled with the economics and technical complexities of manufacturing the material.

The deterioration of cellulose ester base film can follow several mechanisms which may occur simultaneously.

- 1. Deacetylation occurs when acetyl groups are removed from the cellulosic polymer chain, releasing acetic acid. Small changes are detectable by chemical and physical tests such as free acidity, copper number, and viscosity. An acidic odor is usually noticeable before any significant changes in chemical, physical, or image properties.
- 2. Depolymerization refers to breakage of main molecular chain lengths. This is reflected in decreased mechanical properties.
- 3. Plasticizers and residual solvents are released from the base which results in reduced flexibility and moisture resistance.
- 4. The bond between the support and emulsion may fail causing the emulsion to wrinkle. This is a result of the base shrinkage caused by deacetylation and depolymerization.

Several environmental factors can be listed as playing an important role in the degradation process of cellulose acetate film. They are:

- 1. Relative humidity which causes hydrolytic degradation, resulting in deacetylation;
- 2. Heat which causes thermal degradation; and
- 3. Fumes in the environment, such as from deteriorating cellulose nitrate film. This can initiate decomposition.

There is widespread agreement that hydrolytic degradation plays a dominant role in practical situations. This has been further supported by the present study which provides ample correlation between humidity trauma and the level of degradation of film base. As so often repeated by the manufacturers, proper storage and processing of the film is essential to the stability of the negatives.

The cellulose molecule, even after its three side hydroxyl groups are fully esterified, has a strong affinity for water and this attraction can be disastrous for the stability of film

During hydrolytic degradation, the acetyl groups split off from the polymer and react with water molecules forming acetic acid. The presence of the acid then causes an autocatalytic reaction in the polymer, causing further splitting of acetyl groups. The action of water molecules is also dependent on the types and quantities of both the plasticizers and solvents in the original formulation of the base product.[33]

Thermal decomposition takes place in all organic compounds with an increase in temperature. The thermal deterioration of cellulose nitrate is well-documented and understood. Hill and Weber, in tests on controlled samples of cellulose acetate and cellulose nitrate, demonstrated the superior stability of the acetate products in various accelerated oven-aging treatments.[34]

One other factor which has proven to dramatically affect the stability of cellulose acetate film is the presence of deteriorating cellulose nitrate film. Carroll and Calhoun (1955) clearly proved that nitrogen dioxide, even in small quantities, is seriously damaging to safety film. Nitrogen dioxide is released through the deterioration of cellulose nitrate film and combines with moisture to form the very reactive nitrous and nitric acids. They in turn degrade the cellulose acetate film. As expected, the rate of attack increases with an increase in relative humidity. The degradation includes the cleavage of cellulose chains to lower molecular weight (depolymerization) and splitting acetyl groups from the cellulose

acetate polymer. A change in molecular weight is detected by a decrease in intrinsic viscosity and the deacetylation is determined chemically.[35]

In addition to these three causes of degradation, which are considered environmental factors and which have been discussed in the literature, there are other factors and combinations of materials which could play an important role in the process and explain why certain negatives degrade before others in the same environment. The complex interdependency of inherent factors in the film base, such as solvent and plasticizer content, initial components of the esterification process and casting "dope", and environmental variables can only be discussed in general terms with some degree of speculation.

Technical literature relating to these variables is almost nonexistent.

Theoretical studies specifically discussing the depolymerization and acetylation of cellulose acetates are also rare. The work of the Russian photo chemist Kozlov in the 1930s, while quite dated in many ways, nonetheless provides some discussion of the aging and degradation of cellulose ester films, including both acetates and nitrates. He discussed the various aspects of depolymerization which he considered to be a major factor in the aging of cellulose ester films. Kozlov also described his studies showing the interrelation between plasticizers, composition and proportion of solvent mixtures, and the conditions of manufacture on the deformation of cellulose ester films.[36]

In a 1981 study by Adelstein and McCrea, the relative stability of polyethylene terephthalate was compared to cellulose triacetate in terms of its chemical stability during long term storage under various conditions. Their testing predicted that under recommended storage, polyester-base films will retain acceptable physical properties for several thousand years and cellulose triacetate for at least 300 years. The study also describes experimental procedures and testing standards for these materials.[37]

In a work primarily about the aging of cellulose paper products, George Richter and Frank L.

Wells pointed out the critical effects of various additives in the aging of cellulose: "since most types of cellulose products contain other components that are added deliberately to develop properties that are not inherent in the cellulose itself, the progressive chemical attack of these substances or of intermediate

reaction products of these additives on the cellulose can play an important role, [an] example is the influence of plasticizer material often used in the manufacture of cellulose ester products."[38] This echoes the previous statement by Stannet commenting on the difficulty in preventing the depolymerization of the cellulose acetate molecule.

Variables in the manufacturing process are, of course, impossible to document. Extensive quality control procedures and thorough testing of materials before, during, and after manufacturing at the Eastman Kodak Company have been highly praised in the industry and the results of the present study show that effort in the current condition of most Kodak film products. Some Agfa/Ansco and Dupont Defender film fared less favorably especially in the period immediately following WWII and ending with the introduction of polyester film in the 1950s. Obviously certain variables and uncertainties exist with these historical materials.

As described in Section 2, the manufacture of cellulose ester film base includes various choices and tolerances, all of which are set, within certain limits, for each product being produced.

Calhoun states that "in all industrial operations certain manufacturing tolerances are unavoidable and the production of photographic film is no exception."[39]

Other variables which could have an effect on the aging of cellulose ester film negatives are the conditions of handling and photographic processing. There is evidence that the type and composition of the enclosure material may be an important variable. Processing is not thought to be a major consideration since residual processing chemistry would be evident from staining and image degradation. However, it is possible that any handling and processing variables may have only a subtle effect on the image, or the base could degrade before any image change would have occurred.

#### **SECTION 4 – METHODOLOGY**

The prime focus of this study was a survey of film collections and a determination of the extent of cellulose acetate degradation. Institutions were selected for the survey based on their holdings of negatives from the period 1925-1955. Collections included had accurate documentation for the dates of particular negatives available either directly on the negative sleeves or through the use of indexes or other finding aids. A variety of collections were included in the sampling to get the best possible variety of film types, uses, and formats. Institutions were also selected which presented a variety of storage and environmental conditions.

The site surveys themselves consisted of two steps. First, worksheets were completed for each collection. Entries were made on the worksheets for negatives which fit the project's chronology. Samples were included for both degraded and nondegraded examples and for all manufacturers and film types (notches) represented. The total number of samples would vary with each collection depending on the arrangement of the negatives, the size of the collection, and the ease of dating particular samples. The worksheet, a sample of which is given in Appendix A, contains the following items of data:

**COLLECTION/NEG** # This column was used to record a collection specific number for each individual sample included. A two to four letter prefix designating the institution was included with the institution's own negative number (location).

MANUFACTURER & NUMBER The manufacturer of a particular negative sample was recorded here with any number that appeared embossed in the film edge with the manufacturer's name. This number, referred to as the "machine number," is generally considered to be the number of a particular notching machine used in the finishing of the film. Historically, these numbers have been used by various manufacturers to follow the movement of raw film stock, or to indicate the number of an inspector of a particular film batch. More recently Kodak has used the number to identify the film product itself.

**NOTCH** Film notch codes are cuts on the edges of sheet film that canbe used to identify the film type, as well as locate the emulsion side of the film when film holders are loaded in thedark. The sample's "NOTCH REFERENCE" (see Appendix B) was recorded or, if not known, the actual notch was carefully traced in pencil. A notch reference would then later be assigned.

**NOTCH REFERENCE** A unique alphanumeric designation was assigned to each notch. For Kodak negatives this reference refers to Kodak's own notch designation as recorded by their Patent Office. This was useful for their own records and keeping track of notch usage and chronology. Unfortunately, these records are not available from other manufacturers. For these examples a notch

reference designation was assigned for this survey. A listing of notch references is included in Appendix B.

**LEVEL OF DETERIORATION** Each negative was assigned a number from 1-6 describing its physical condition at the time of the survey. These six levels can be described as follows:

Level 1-- No deterioration; flat negative.

<u>Level 2</u>--Negative exhibits slight or moderate edge curl with smooth surfaces on both emulsion and base sides. Edge curl is always symmetrical on the two or four sides affected.

<u>Level</u> \_3--Smell; the negative smells distinctly of acetic or butyric acid. This determination is difficult to make if there are large numbers of degraded negatives in a confined area such as a box or drawer where the acid odor permeates. Usually in these cases there is level 4-6 degradation evident as well.

<u>Level 4--</u>Warpage; wavy portions in edges and surface of the negative; not symmetrical; no separation of emulsion or base. One of the first signs that a negative may be degrading is that it will show signs of warpage. Slight warpage or deformation can also be caused by the uneven loss of solvents from the negative. The type of warpage which indicates serious degradation is most often verified by the existence of other further degraded samples in the immediate vicinity of the warped negative.

<u>Level</u> 5--Bubbles; occasionally when an acetate negative degrades, bubbles may form between the emulsion and base or between the base and the anti-curl backing of the film. These bubbles vary in size and may appear in a circular pattern from the center of the negative out to the edges. Occasionally these bubbles are filled with a volatile liquid.

<u>Level 6</u>--Separation of the emulsion, base, and anticurl layers. This can be evident in varying degrees, from slight localized separation to massive separation. A white crystalline exudate is often seen under the separated portions of the base material. This substance is most likely to be the plasticizer used to manufacture the film base such as triphenol phosphate.

**DATE** This column was used to record the date of the negative as closely as it can be determined from the photographer's records. To be included in the final data analysis, the date should be reasonably verifiable within a year.

**FILM THICKNESS** Initially the thickness of each negative sample was recorded using a dial type calipers. Little variation was noted between the sheet film negatives in various conditions, with thicknesses ranging from .008 to .010 inches in all samples in various conditions. After several site surveys this measurement was discontinued.

**FILM SIZE** The nominal size of the sheet film being sampled.

**NOTES** Observations were recorded here for any special conditions of a particular sample, including additional comments about condition, appearance, or environment, as well as qualifications for date or notch information.

The second portion of the site or institutional surveys consisted of an interview with the curator or caretaker of the collection to record the storage and environmental history of the material surveyed. This information would include, if known, how and where the negatives were stored before they arrived at the institution and the same information for the institution's own storage.

Of particular interest would be any trauma the collection may have suffered, such as fire, flood, or warehouse storage, that would effect the present condition of the negatives.

Data recorded on the worksheets was entered into a computer where it was sorted and analyzed as

described in Section 6.

#### **SECTION 5 - COLLECTIONS SURVEYED**

#### The Library of Congress, Washington, D. C.

The Historic American Buildings Survey (HABS) Beginning in 1934 the Library became the repository for the records of the Historic American Buildings Survey. The survey, designed to document America's architectural heritage, includes many photographs taken at various sites throughout the country. The photographs were taken at the request of various regional field directors of the project by both amateur and professional photographers. They are presently filed geographically by state and county.

Most of the HABS negatives came to Washington within the year after they were taken. They were first stored on the south deck of the Jefferson Building where there was no air conditioning until the mid 1960s. The windows of this building were often left open because of excessive sunshine and heat in the summer. The humidity of the storage environment matched that outdoors on those occasions. In the early 1970s the collection was moved to the Adams Annex which had a very primitive air conditioning system. The staff described great extremes in both temperature and humidity in that location. The present storage situation in the Madison Building is more consistent and close to accepted standards.

The HABS Collection contained a quantity of nitrate film which were interfiled with the safety film. "Soft prints" (low contrast) were made from these negatives and copy negatives were made.

The Carnegie Survey of the South contains the work of Frances B. Johnston. Approximately 8,000 of her negatives dating from 1926 to 1942 are part of this collection. The Johnston negatives are significant for this project since she deliberately utilized the "new" safety film available from Kodak after 1925 to avoid the preservation problems of nitrate negatives. The dates of many of the early Johnston negatives are not exact but it is assumed that most of the HABS negatives taken before 1933 are by Johnston. No dated examples before 1930 show any signs of degradation other than some yellowing. Her negatives were stored in her New Orleans home for at least ten years before they were added to the library's Collection.

The Arnold Genthe Collection A small portion of the Arnold Genthe Collection between 1926 and 1936 were included in the survey because of the existence of early degraded samples. The collection was acquired by the Library in 1943. Before that it was stored in New York City. Nitrate negatives were originally interfiled with the safety film but were later removed and stored separately.

<u>The Gottscho-Schleissner Collection</u> See separate description of this collection.

#### Syracuse University Library, Special Collections, Syracuse, New York

The Clara Sipprell Collection Clara Sipprell was a very respected portrait photographer who specialized in sensitive soft focus portraits. Her negatives surveyed cover the period 1926-1953. It is believed that the collection was stored without air conditioning in the home/studio of the photographer before it came to Syracuse. She lived in Buffalo, New York and Manchester, Vermont. Nitrate negatives were interfiled with safety film throughout the collection.

The collection was received by Syracuse during the period 1975-77 where it has been stored in the stacks of The Special Collections Department. Temperature and humidity are not currently monitored but it is thought that there is some variation from accepted standard but without extreme shifts in either value. The negatives, originally stored in kraft paper envelopes, are now interleaved with acid-free buffered paper.

The Margaret Bourke-White Collection Several thousand of Bourke-White's negatives dating from 1929-1938 were surveyed. They include mainly 4x5 and 5x7 commercial negatives which had been stored in glassine sleeves. They came to Syracuse in 1972-73. Before that the negatives were stored at the photographer's home in Darien, Connecticut. It is believed that a portion of this negative collection was stored in the garage. Nitrate negatives were originally interfiled with the safety film.

#### The Indiana Historical Society Library, Indianapolis, Indiana

The Martin Collection Approximately 30,000 negatives dating from 1937-1949 were surveyed for this project. The Martin Studio of Terre Haute did general commercial and some portrait photography. Before coming to the Library, the negatives were stored in a wood frame, brick veneer building, shelved and sleeved in glassines. The negatives were located against an outside wall and suffered from seasonal extremes in heat and humidity. The collection originally contained large quantities of nitrate and glass plate negatives but a fire in the building caused extensive losses. The collection is complete only after 1940.

#### The Florida State Archives, Tallahassee, Florida

Several collections from the Florida State Archives in Tallahassee were surveyed by their staff and included in this project. Their data was particularly interesting because of the relatively large number of degraded negatives in their collections and the percentage of their collections affected.

<u>The Spottswood Collection</u> Gordon Spottswood was a Jacksonville commercial photographer whose collection dates from about 1920-1967 and contains 25,000 sheet film negatives. Most of the film is safety base although nitrate film was originally interfiled. Before coming to the Archives in 1980 the collection was stored in an unair-conditioned environment.

<u>The Jacksonville Journal Collection</u> 25,000 safety base sheet film negatives were included in this collection which dates from 1951-1959. It too was not stored in an air-conditioned environment before coming to the Archives.

<u>The Fishbaugh Collection</u> William Fishbaugh was a commercial photographer from Miami whose negatives date from 1920-1935. The collection originally contained mostly nitrate negatives (about 15,000) which were printed and destroyed after the collection came to the Archives in 1955.

Since 1982 these collections have been stored in the vault of the State Archives which has temperature and humidity controls of 72 degrees and 68% RH. Summertime values, however, have been observed to fluctuate well beyond those specifications.

#### The National Museum of American Art, Washington, D.C.

<u>The Juley Collection</u> contains mostly large format copy negatives made from works of art. Juley operated his studio in three separate locations in New York City from 1896-1975. At one point there was a fire at the Juley Studio and the collection suffered some smoke and water damage. During the period 1975-82 it was moved to several locations in the Washington, D. C. area. Some of those locations were air-conditioned and some were not. At one of these locations there was a water leak and the collection suffered some further damage. Also, part of the collection was stored for a time in an uncontrolled, nonventilated area where temperatures rose to over 100 degrees F. Nitrate negatives had originally been interfiled in portions of the collection, but were removed and stored separately in Washington.

In 1982 the collection was put into a cold storage facility which has controlled a temperature of 45 degrees and 35% relative humidity.

Although the Juley negatives are not easily dateable, there are many examples of base deterioration with a wide variety of film types, including those types used for photographing works of art. The collection also has a well-documented storage history.

#### The National Archives, Still Picture Division, Washington, D.C.

The following collections were surveyed for inclusion in this project:

The Forest Service Photo Collection, RG 95-G This large collection totaling over one half million negatives dates from 1889-1965. It includes photographs taken by Forest Service photographers and other employees in the field during the course of their work. Most of the negatives appear to be on sheet pack film, both safety and nitrate. The nitrate negatives are interfiled with the safety negatives. There is evidence of deteriorated safety film primarily during the 1934-1939 period when both safety and nitrate were being used and interfiled together.

For many of the collections at the National Archives, the storage history of the record group at the originating agency before it came to NARS is not usually known. However, in the case of the Forest Service, the "Appraisal Report on Transfer Offer" states the following: "the negatives were stored for several decades, unjacketed, packed tightly together in the attic of the South Agriculture Building which is an unheated, unairconditioned area. They have already been subjected to excessive variations of heat and cold, and [the nitrate negatives] have not deteriorated."

WPA Information Division Photographic Section, RG 69-N This collection contains approximately 25,000 negatives showing a wide variety of WPA activities from 1935-1939. Before 1950 the collection had been held by the General Services Administration at the Old Interior Department Building in Washington. Specifics about its storage environment are not known. This file at the National Archives is jacketed in its original kraft paper sleeves. Many of the degraded acetate negatives show clear signs that the separation of base and emulsion follows the seam lines of the sleeves. The collection originally contained many nitrate negatives interfiled with safety film. Many of the nitrates have been duplicated onto safety film.

The Army Still Photography Collection, RG 111-SG A portion of the Army Collection dating from 1944-1954 was surveyed and found to contain degraded safety film. There were no nitrate negatives found within the series. The negatives are all on 4 x 5 inch sheet film stock. The photograph collection was stored at the Pentagon until about 1982 when it was transferred to the Naval Photo Center (Defense Audio Visual) at Anacostia. In 1986 it was moved to the National Archives Building. Specifics of its storage environments is not known but it is thought to have enjoyed relatively consistent storage throughout its history.

<u>The George Washington Bicentennial Commission Photographs, RG 148-GW</u> This small group of photographs includes negatives prepared for the George Washington Bicentennial Commission during the course of their work in 1931-32. The collection was transferred to the National Archives Building in

1955. Previously, it had been stored at the Federal Hall Memorial Museum in New York City. The safety negatives in the file exhibit considerable deterioration. Nitrate negatives are interfiled throughout the series.

It should be noted that the present storage environment at the National Archives is relatively stable with temperature near 70 degrees F and relative humidity at 50%. In the past, the building did not have an in-house maintenance program and the environmental conditions were somewhat worse.

The National Archives Cartographic and Architectural Branch Alexandria, Virginia. Several degraded negatives dating from 1937 were found in the Cartographic Section. They were 8 x 10 and 11 x 14 standard sheet films used for aerial indexing purposes, that is, they are copy negatives made of composite aerial prints. After surveying some of the aerial film roll stock, no degradation was observed. The Assistant Chief of the section reports that he has never seen a deteriorated safety-based aerial film negative.

#### Temple University, Philadelphia, Pennsylvania (TU)

The Philadelphia Inquirer Collection Two million negatives dating from 1937-1956 were surveyed from this newspaper morgue file. The storage history of the negatives indicates a wide variation in environmental conditions. The negatives were stored at the newspaper offices (with seasonal air-conditioning) until the late 1950s when the collection was moved to a storage warehouse in north Philadelphia which was not heated or airconditioned. In the early 1970s there was a fire at the warehouse and the negatives suffered some smoke and water damage. The file was moved to Temple University in 1979 where it was stored in a nonair-conditioned environment. In 1983 it was placed in its present storage in the Paley Library where it enjoys some temperature and humidity control and little radical fluctuation in those values.

Of particular interest in this collection was the wide range of deterioration evident even within a narrow chronology and particular film type. There was ample evidence in the collection of staining which might indicate water damage or improper processing. Also, many of the negatives were stored in kraft paper sleeves and were filed with newsprint caption sheets directly adjacent to the film surface.

#### The Historic New Orleans Collection, New Orleans, Louisiana

The Clarence John Laughlin Collection This collection by the well-known New Orleans art and architectural photographer, Clarence John Laughlin, contains a relatively high percentage of degraded negatives, primarily on his preferred Agfa/Ansco film. Laughlin's collection, which dates from 1932 to the late 1960s was stored in the artist's attic apartment in the French Quarter in New Orleans. The environment was unregulated and subject to the extreme temperature and humidity conditions so common in New Orleans. The negatives were stored in glassine sleeves. From 1968-81 they were stored at the University of Louisville Photographic Archives where they enjoyed an air-conditioned environment with relatively low year-round humidity. From 1981-83 humidity control presented a problem for the Archives and extreme summer humidities of 80% and higher were not unusual. In 1983 the negatives were transferred to the Historic New Orleans Collection where they are stored at 68 degrees F and 50% relative humidity.

The Charles L. Franck Collection contains sheet film negatives dating from 1915 to 1955 taken by Franck for his commercial studio. They were originally stored by the photographer at his studio in downtown New Orleans in metal filing cabinets and cardboard boxes. The environment was not controlled except possibly for some seasonal air-conditioning during the later years. Some of the negatives were sleeved in kraft paper envelopes and others were not sleeved. Nitrate and safety film were interfiled. The collection came to the Historic New Orleans in the spring of 1979.

Approximately 100,000 negatives from the <u>Keystone Mast Collection</u> dating from 1926-1953 were included in the survey and very few degraded negatives were encountered. The negatives in this well-known collection of stereo views measure slightly smaller than 5 x 7 inches. There is considerable nitrate material in the collection but these negatives are not interfiled with safety negatives.

The collection was stored in an old school facility in Meadville, Pennsylvania from 1924 until about 1977. While there was no air-conditioning in the building, it is thought that its temperature and humidity conditions were moderate and consistent. In 1977 the collection was moved to Fresno, California and in 1979 to the Museum in Riverside. At present there are no special air-conditioning facilities for the Museum, but a new building is being planned.

#### The San Diego Historical Society, San Diego, California

The two negative collections surveyed at the San Diego Historical Society are in very good condition. These collections contained a small number of deteriorated negatives. The <u>Union Tribune</u> collection, dating from 1938-1953, was stored at the newspaper office in San Diego without air-conditioning until 1955 when it was moved to the Pacific Title Insurance Company. It was air-conditioned until 1983 when it was moved to the Historical Society Building in Balboa Park, San Diego along with the Insurance Company's own vast collection. While the present facility does not have a functioning temperature and humidity control system, the society has stored its negative files in a cold vault with a temperature of 55 degrees F and 45% RH.

# **University of California, Los Angeles, Special Collections**

The primary collection surveyed at UCLA was the <u>Los Angeles Dally News</u> file dating from 1936-1954. The collection was originally stored at the newspaper in downtown Los Angeles and later in the basement of the Los Angeles <u>Mirror/News</u>. In the early 1960s the collection was given to UCLA where it was stored in the old Clark Library. By 1970 it was moved into the Powell Library where it enjoyed some air cooling, but fluctuating humidity levels. It was stored in its original cardboard boxes and kraft envelopes until a resleeving project was started in 1980.

A smaller collection, from the studio of Adelbert Bartlett of Santa Monica was also surveyed. Its storage history is not known but it contained no degraded samples.

#### Arizona State University, Special Collections, Tempe, Arizona

Collections surveyed at Arizona State University include <u>The Kelley Collection</u> in the University Library and <u>The Archives Collection</u> from the University Archives. These collections were included in the survey because of the reported sudden onset of deterioration in an environment which generally tends to be quite dry. An interview with the head of the Archives and Manuscripts section revealed that each collection had suffered at least one temperature and humidity "trauma" in its past.

In the case of the R. F. Kelley negatives, a commercial collection which dates from the early 1940s to the middle 1950s, this trauma probably began when the negatives were stored in an old firehouse for several years in the mid-seventies before they were were given to the University. This warehouse reportedly had a leaky roof and the ASU staff describes destroying many deteriorated nitrate and acetate negatives before they were moved to the University Library. In the summer and fall of 1983, a slow leak began in the roof of the Library which eventually damaged boxes containing Kelley negatives. More degradation was noticed soon thereafter. Many of the Kelley negatives exhibit water damage and damage caused by the seams of envelopes which had been wet. The Hayden Library

Building, which houses the Kelley Collection today, is supposed to be both temperature and humidity controlled, although this is doubted by the staff.

The Archives collection also saw a dramatic increase in the number of deteriorated negatives in late August 1983. In July the carpeting in the room containing the negative file was washed and left very wet. The window air-conditioning was turned off for the weekend. Arizona summertime temperatures can fluctuate from 78-105 degrees and humidity from 20-60%. The negatives, which had been looked at as recently as the previous spring, began to show rapid deterioration. It was estimated that 410,000 degraded acetate negatives were disposed of. In January 1984 degrading negatives were placed in a freezer. These negatives, mainly from the 1947-55 period, were originally from the University's Bureau of Publications.

#### The Museum of the City of New York

See The Gottscho/Schleissner Collection

#### Columbia University, Avery Library, New York, New York

See The Gottscho/Schleissner Collection

#### The American Museum of Natural History, New York, New York

Approximately 30,000 negatives from the Museum's study and research collections were surveyed. The 4 x 5 negatives showed almost no degradation, with only a few degraded items showing up in the 8 x 10 negatives. As expected in a primarily scientific and research collection, many glass negatives were included. Nitrate negatives had been copied onto safety base negatives and removed.

This collection seems to show the positive effects of consistent arrangement, description, and especially storage. According to the staff of the museum, these negatives usually came to the museum very shortly after they were taken by the photographer/scientist during a particular project or expedition. To the best of their knowledge, the storage environment has been air-conditioned for many years.

## The University of Louisville Photographic Archives, Louisville, Kentucky

Several commercial studio collections were surveyed for the project. The largest, <u>The Caufield and Shook Collection</u>, contains several hundred thousand negatives dating from the period 1925-1955. Most of the collection consists of 8 x 10 inch sheet film.

The collection had been given to the University in several installments beginning in 1968. Before that it was stored at the studio in downtown Louisville in a nonair-conditioned environment. Louisville's summertime humidity can be very inconsistent and 90% RH is not unusual. After the collection was moved to the University, it was stored in a building with adequate air-conditioning and a generally low year-round humidity. Some degraded negatives were noticed in the collection as early as 1975. In 1981 the Archives was moved to a new building which proved to have very inadequate environmental controls which allowed humid summer air to be mixed with building air thereby causing radical fluctuations in the humidity levels of the stack areas. Shortly after the move to the new building, the staff noticed a marked increase in the number of degraded acetate negatives in this collection. The negatives are being resleeved in buffered paper jackets but most of them remain unsleeved, grouped in batches of 100 negatives. The studio made a quick transition from nitrate to safety in about 1930, so there was very little interfiling of nitrate and safety film, but the nitrate portion had been stored in the same storage facilty.

Another Louisville commercial studio collection was also surveyed. <u>The Royal Photo Studio</u> operated during the same period as Caufield and Shook. The collection was stored without air-

conditioning until it came to the University of Louisville Archives in 1981. The negatives have been heavily weeded and many degraded examples were disposed of, including the nitrate and glass negatives.

#### The Gottscho/Schleissner Collection, Various Locations

This collection provided a fascinating case study for this project with compelling evidence that early storage conditions of a particular group of negatives determine their condition later in their lives.

Samuel Gottscho was a very prominent and accomplished architectural photographer who operated a studio in Jamaica, New York from about 1925-1972. He was later joined by his son-inlaw, William Schleissner. Beginning in 1954, the photographers divided the collection into portions which were transferred to several institutions based on their particular collecting interests. The Museum of the City of New York received New York City photographs dating from 1925-1940. The Avery Architectural Library at Columbia University received negatives from the same period covering more general architectural subjects. The Library of Congress received a smaller portion from the 1925-40 period but a large group of negatives dating from 1940-72. Also, Mrs. Doris Schleissner, the daughter/wife of the photographers, still retains a series of negatives for continued publication use. These negatives were all from the same numerical and chronological sequence with the original numbering retained by each institution.

The negatives were originally stored in the basement of the photographer's home in New York. Conditions there were not documented but it is assumed that like typical basement storage, the temperature was normally low and the humidity high. Kraft paper sleeves were originally used for the whole collection. Environmental conditions at the various collection sites have varied since the negatives were added to their collection. No particular temperature or humidity traumas were reported other than moderate fluctuations in their storage environments. The Library of Congress has resleeved the negatives, and the Museum of the City of New York has added a glassine sleeve inside some of the kraft envelopes. The Avery Library has used rubber bands to keep groups of related negatives in their original sleeves.

After analysis and comparison, each portion of the Gottscho collection contains examples of degraded negatives from matching number and chronological sequences. Film manufacturers and film types also match. This case study is compelling evidence that the conditions for degradation preexisted before the distribution of the negatives to the various collections. Later storage and environmental conditions, although somewhat varied, did not greatly affect the present condition of the degrading negatives. It is not known how the later conditions affected the <u>rate</u> of degradation, however, and it is possible that more favorable conditions may have slowed the process somewhat.

#### **SECTION 6 - COMPILATION OF RESULTS**

Sixteen institutions were surveyed. Twenty-nine individual collections were inspected and a total of 3396 negatives were sampled. Only safety-based sheet film was sampled for this project. Most of the negatives surveyed were considered "professional" or "portrait" films and few graphics arts type films were encountered. Aerial and other roll film stock were not included. The results of the survey are shown in Figure 1 and Tables 1-4.

The earliest dated Kodak safety film was 1926. Agfa safety film samples dated from 1936. Defender safety film dated from 1934-1945 and Dupont Defender from 1945-1955. Only several samples from the Hammer Company were encountered and these dated from 1946-48.

Table 1 lists the various film types sampled with notch references taken from Appendix B. Also listed are the total number of collections which contained degraded samples of that film type, as well as the dates from which degradation was most evident. A specific film type was not included on this list where less than five samples were encountered. Samples of several Kodak film types, including Super Sensitive Pan (Notch 4G) and Portrait Pan (Notch 3C), for several years during the 1936s were found to be degraded in moderate percentages in the majority of collections. A very high percentage of Dupont Defender film dating after 1945, particularly notches A, B, and C, were found to be degraded in almost every collection surveyed. Agfa/Ansco film types appeared degraded in moderate percentages throughout the chronology, although the total number of different collections containing this film was relatively small, making comparisons problematic.

Table 2 totals the number of film types (notches) for each manufacturer and the number of those film types which have degraded samples. All manufacturers' negatives show a high percentage of film types which have degraded, that is, most cellulose acetate-based sheet film can be affected in the same way. Table 3 shows the total number of negatives sampled and listed by manufacturer. This indicates the percentage of samples from each manufacturer that were degraded. Again, with the exception of Dupont

Defender (post 1945) film, percentages for each of the manufacturers were relatively close, varying from 19-38% of the total sampled.

It should be noted that the percentages cited in this compilation are useful only in relation to each other in the specific context of this project. This is due to the sampling method which was heavily weighted toward suspect collections and areas within collections. These figures are not to be extrapolated to collections of materials not sampled. For example, most collections will contain far less than the total 30.9% degraded samples for this survey. A very large collection may contain only a small percentage of degraded negatives. The University of Louisville's Caufield and Shook Collection, for instance, contains roughly 5000 degraded negatives out of a total of approximately 160,000 negatives, or 3.1%.

Percentages can also be somewhat deceptive in instances where few samples were registered, such as for Hammer film.

A useful summation of the data is seen in a chronological overview for each manufacturer of the total number of negatives surveyed and the number of degraded samples. This data is tabulated in Table 4 and graphed in Figure 1.

Figure 1 shows a comparison between manufacturers and the percentage of degraded samples. It indicates the average for all samples, as well as that for individual manufacturers. Regardless of data skews caused by sampling size, general trends remain consistent. Kodak film accounts for all of the degraded samples dated before 1936. After 1936, the total percentage for all negatives becomes an average of the three major manufacturers individual percentages. After 1940, the Kodak average fell consistently below the mean, while Agfa/Ansco and Defender films suffer from higher than average percentages of degradation.

It is interesting to note that pre-1930 samples of Kodak safety films show no signs of serious degradation. This is despite the fact that these films are most definitely on cellulose diacetate film base. The early samples were part of collections which contained other later degraded samples. Later degraded Kodak films, especially those dated after 1940, were probably made with one of the mixed

cellulose esters. Both Agfa/Ansco and Defender/Dupont Defender products were on cellulose diacetate film base throughout the period. This indicates that all cellulose esters are susceptible to degradation and not just diacetate as had been assumed by some curators. Conversely, negatives still in good condition include diacetate, as well as the mixed esters.

Although some degraded Defender films were dated before 1945, there was a clear increase in the percentages of degraded film after 1945, the year that Dupont assumed control of the company. [40] For instance, notch K Defender film (X-F Panchromatic) dated 1934-41 was found degraded in only one of ten collections which contained them. Later Dupont Defender film, such as notches A, B, & C from the 1946-1955 period were found degraded in nearly 100% of the samples surveyed.

A comparison of film shrinkage by various manufacturers was recently undertaken by Ira Current, former manager of Photographic Engineering, Products Specifications at Ansco. He measured negatives from his own collection and found that Kodak and Agfa/Ansco products show a more "normal" average shrinkage (based on nominal widths specified in ANSI-PH1.18-1956) than Defender films which averaged well above the "normal" degree of shrinkage.

Insert Table 1 (landscape)

**Insert Tables 2-3** 

Insert Table 4 (landscape)

Insert Figure 1 (landscape)

## **SECTION 7 – CONCLUSION**

"The history of a cellulose derivative can never be completely known, and so the exact behaviour of a given sample cannot be precisely predicted or explained." Vivian Stannett, <u>Cellulose Acetate</u>

<u>Plastics</u>, 1951.

This statement best describes the difficulty in discussing the problem of deteriorating safety-based photographic negatives. As described in Chapter 3, the number of technical and storage variables make exact explanations extremely difficult. Each collection is different in terms of storage histories, present storage conditions, enclosure materials, the presence of nitrate film, and other specific factors. It is interesting to note that only portrait or professional sheet film and some rare examples, of motion picture film have been found to be degraded. No aerial or color film and only one sample of 35mm roll film were found to be degraded in the collections surveyed. All of these film types were produced on basically the same film bases as other sheet film. Possible explanations may include the following:

- 1. Portrait sheet film has a thicker base facilitating better retention of acidic by-products of degradation, thereby increasing the autocatalytic nature of the process.
- 2. Aerial film bases are thinner and contain no anti-curl layer. Consequently, acidic by-products could escape from the back side. As described in Chapter 3, manufacturing tolerances, especially for residual solvents are extremely tight to minimize dimensional change.
- 3. Color films have thicker emulsions. The emulsion itself is known to have a moderating influence on the stability of the film laminate by absorbing acidic by-products.[41]

Several other generalities are obvious from an analysis of the data. First, some individual collections contain a far greater number of degraded samples than other collections and some institutions contain more of these degraded collections. The following are the major factors which relate directly to the condition of negative collections:

- 1. temperature and humidity history;
- 2. storage of nitrate negatives with safety film;
- 3. storage in acidic sleeving material; and

4. the microenvironment of the negatives.

## **Temperature and Humidity History**

Given the well-documented susceptibility of cellulose acetates to hydrolytic degradation, it is no surprise that the temperature and, more importantly, the humidity history of a collection plays a major role in the present state of preservation of a negative collection. Many of the collections faced with serious degradation were produced and/or stored in geographic areas with a high average relative humidity or the specific storage history of individual collections has included some degree of temperature and humidity trauma at some point in their lifetime before arriving at an institution.

Collections stored in geographic areas with low relative humidity and infrequent drastic fluctuations have generally fared much better. These include collections in California and Arizona.

Certain film types, mainly Dupont Defender, degraded in these locations as well, but most acetate film is still in relatively good condition in these collections. On the other hand, collections and institutions located in areas of high average relative humidity contain far more degraded negatives of all types and manufacturers. The Florida State Archives, the University of Louisville, the Historic New Orleans Collection, and several collections in Washington, D.C. are good examples.

Collections stored "properly" without extremes in temperature or humidity and without significant "trauma" also seem to contain far fewer degraded examples of all types and manufacturers. Most notably in this category is the collection at the American Museum of Natural History. Although the collection contains a large number and variety of film types of several sizes, taken by many photographers on locations throughout the world, the collection is in very good shape with only one small pocket of degraded negatives. Neither temperature or humidity has been accurately controlled at the AMNH, but conditions have been kept moderate and consistent.

Humidity and moisture also played a key role in at least one example of rapid degradation of negatives. The situation at the Arizona State University Archives when the carpet was washed and the room reached a very high level of humidity as described in Section 5, dramatically illustrates that point.

Prior to this event the negatives were not stored in a sophisticated temperature and humidity controlled environment, but conditions were considered "moderate." It was the radical change in humidity that was an important factor in causing the sudden onset of degradation.

A major change in the average relative humidity with frequent peaks over 80% also seemed to be a causal factor in the rapid increase in the degradation of negatives at the University of Louisville Photographic Archives.

Other collections which contain degraded negatives have histories which often include other forms of moisture trauma, such as fire or flood. The collections which were affected by such occurrences included the Kelly Collection at Arizona, the <a href="Philadelphia Enquirer">Philadelphia Enquirer</a> Collection at Temple University, and the Martin Collection at the Indiana Historical Society. The early basement storage of the Gottscho collection may have "predisposed" certain negatives eventually to degrade at the various institutions at which they are housed.

## **Storage of Nitrate Film**

Another factor which plays a major role in the process of degradation is the storage of cellulose nitrate negatives in the same or adjacent storage areas. These effects are well-described by Carroll and Calhoun in their study "The Effect of Nitrogen Oxide Gases on Processed Acetate Film". They concluded that the combination of nitrogen oxides and high humidity are particularly damaging, a fact that has particular relevance for the collections surveyed. Collections which had nitrate negatives actually interfiled with safety film, such as the Clara Sipprell Collection, were particularly adversely affected. Storage of nitrate film in collections such as the University of Louisville's may have contributed to the degradation of the safety film samples. Some collections which contained degraded safety film did not have nitrate film stored with them, so this factor, while important, is not the only element which encourages degradation.

### **Storage Enclosures**

A third storage-related condition frequently encountered with these collections was the presence of improper filing enclosure materials. Kraft paper, glassine, and highly acidic negative envelopes

generally seem to accelerate the process of deterioration. Many degraded negatives begin to show separation of the base and emulsions along the seam of these envelopes. Negatives stored in glassines often show signs of degradation before similar unsleeved negatives or those in paper sleeves.

## The Microenvironment

The physical microenvironment of each negative may also be important to the <u>rate</u> of degradation. More evidence needs to be collected concerning the effects of sleeving a collection of previously unsleeved negatives. Normally the storage of degrading negatives unsleeved in bundles or packs will increase the autocatalytic reactions in the container, and effect more of the surrounding negatives. However, sleeving may appear to increase the rate of the degradation of particular negatives. This seems to be evident in a number of cases as related by collection curators, where previously unsleeved negatives, boxed or bundled in stacks, were sleeved, and the degradation seemed to speed up. This may be due, in part, to the fact that "looser" sleeving provides more surface exposure for interaction between the negative and moisture, oxidizing pollutants, and, perhaps most importantly, with gaseous acetic acid produced by cellulose acetate degradation.

Currently there is not enough data to predict whether sleeving will accelerate or decelerate the rate of deterioration of negatives that have already begun the degradation process. Further observation and investigations are required to help make the decision as to the appropriate action.

These storage and environmental factors are important in that they offer immediate and observable connections which help to explain the degradation of cellulose acetate negatives. No factor can be identified as a single cause of the problem in all cases. More likely it is a combination of these factors which contribute to the autocatalytic process described in Section 3.

But questions must still be asked, such as why do some negatives within a collection which have always been stored together degrade first? Will collections and institutions which now contain a few of these degraded products begin to see similar "pockets" of deterioration in coming years?

The first question can be answered simply by admitting that certain negatives seem to be "predisposed" to more accelerated degradation and susceptibility to environmental factors. This conclusion is supported by the observation that negatives from some manufacturers made during

specific time periods have a very high incidence of degradation. This is most evident in the Defender film manufactured between 1947-1955, and, to a lesser degree, some Kodak film in the 1930s.

It is believed that "pockets" of degradation spread because of the catalytic effect of the degradation by-products which infest more stable materials. It would not be inaccurate to relate this to the "bad apple" phenomenon.

A more exact answer to this question would be speculative without considerable analytical testing of historical negatives. This speculation is made more difficult because of the large number of variables involved.

The second question can be answered with a little more certainty. Given the evidence contained in this report, examples of degraded safety film are widespread, with most institutions surveyed containing a variety of degraded examples from all manufacturers. It is concluded that every institution which contains a substantial quantity of safety film dating from 1925-1955 will find problems with degraded film base somewhere in their collection sooner or later. The extent and breadth of the problem will vary, just as it has with this survey, from institution to institution depending on storage history and the other factors as described in this report.

#### **SECTION 8 – RECOMMENDATIONS**

While the findings of this project reveal certain similarities between collections in terms of storage histories, chronology of degradation, and to a degree, the film types and manufacturers involved, it is necessary to consider each collection and each institution separately to determine a preservation plan. Each collection has a unique storage history and other variables which affect the present condition of the negatives. This accounts for the large diversity between institutions located in different parts of the country and for the variations in the extent of the problem in those collections.

## **Temperature and Humidity Control**

It is not difficult, based on the findings of this survey, to recommend certain measures that are necessary for all collections of cellulose acetate negatives, including negatives dating from 1955-present. First and most important is the maintenance of proper temperature and humidity for the storage of all photographic materials. Cellulose acetate negatives, including all the esters, are extremely susceptible to high relative humidities and their fluctuations. This simple fact is so obvious and so well known to photographic scientists that it has been presented in the literature since the early years of photography. It has been repeated time after time in technical papers, specifications, and various standards. But these instructions have largely been ignored by both photographers and many institutions which house historical collections.

The scare of nitrate film's flammability resulted in strict regulation by the national fire code and forced the issue of cold storage for nitrate negatives. However, the relative stability of safety film, in terms of its promise of longevity, has imparted a false sense of security and many negatives have been subjected to extremely poor storage conditions. Administrators who sidestep the issue of proper temperature and especially humidity contol are asking for more trouble for their negative collections in the future.

Observation of the various portions of the Gottscho Collection indicate that early storage conditions, by the photographer or originating agency, are more responsible for present degradation than more recent institutional storage conditions. Degradation which may have started years ago can dramatically increase in rate with continued humidity trauma. It is believed that degradation can be

appreciably slowed by colder and dryer storage, but it is not believed that the degradation can be arrested once it has started.

Improper storage is not the only cause of serious degradation, but proper temperature and humidity are extremely critical for the long-term storage of all cellulose acetate photographic negatives, past, present, and future. The recommended levels for both medium term and archival storage can be found in American National Standards Institute specification PH1.43-1985. Archival storage requirements recommend 30% relative humdity with little short-term recycling and a maximum temperature of 21 degrees C (70F).

## **Storage of Cellulose Nitrate Film**

As noted, the survey found many collections containing degraded negatives which had nitrate film either interfiled directly or stored in close proximity to the affected collections. The harmful effects of nitrogen oxide gases on safety film is well-documented. Nitrate negatives stored with safety film should be immediately removed to proper storage away from the other collections.

## **Storage Enclosures**

Highly acidic kraft paper or glassine sleeves were shown to aggravate the degradation of many of the negatives sampled during this survey. They should be removed and replaced with paper sleeves or envelopes as specified in ANSI PH1.53-1986.

#### **Monitoring Negative Collections**

This study has not indicated a universal method for identifying negatives which have started to seriously degrade. The correlation of chronology, manufacturer, and notch code identification between collections and institutions can be a useful tool in the efforts to manage a collection of negatives, but at this point, the major emphasis should be placed on the thorough monitoring of individual collections. This method is currently being followed at the Library of Congress, the State Historical Society of Wisconsin, the Florida State Archives, and the University of Louisville Photographic Archives.

In monitoring a collection it is important to realize that degradation is not totally random and that chronologically filed collections dating from 1925-1955 have very clear "pockets" of deterioration. These pockets usually contain negatives exhibiting a range of deterioration levels and may include several film notches and brands. Collections not filed chronologically, but by subject, customer, etc., are much more difficult to monitor because each section or subject is likely to contain degraded samples and the usefulness of chronology is lost. This monitoring process is obviously much more problematic for extremely large collections and for institutions which contain several large collections. Although the percentage of negatives degraded might be relatively small, the total number of affected items might number several thousand. Monitoring procedures should be established and followed for both existing collections and new acquisitions.

When a pocket of degraded negatives is located, typically there will be some negatives with level 6 deterioration (massive separation). The pocket will also contain negatives with less severe warping or smell but that are beginning to degrade. All the affected negatives should be removed from the larger collection. A certain number of negatives on either side of the pockets, which may not show signs of deterioration at present but whose notch, machine number, and/or approximate date matches the more degraded samples, are also suspect and should be removed. The number of suspect negatives will vary depending on the size of the collection being surveyed.

A monitoring method similar to the one used for this survey should be considered since it provides all the information needed to keep track of the degraded portions of a collection. Using the notch reference and worksheets shown in Appendix A and B will provide standard information which can be shared with other institutions and could assist future research into the subject.

Once removed, the negatives should be shelved separately from the rest of the collection, ideally in another part of the storage area. Colder, dryer storage would also be desirable if possible. At this point the negatives must be dealt with quickly since the degradation process can be quite rapid. The following

#### are possible actions:

1. To preserve the informational content of the degraded negatives, prints should be made from them if they do not already exist. This could include the negatives which have separated emulsions since some information may still be printed. Care must be taken in these cases to prevent the emulsion layer from cracking or splitting. These prints should be made with maximum detail and avoiding excessive contrast.

- 2. Duplicates should be made from the negatives in stage 3-4 deterioration and from the group considered "suspect." The question of how quickly this should be done is difficult to answer. With some negatives the final stages of degradation proceeds relatively slowly (months), while in others very quickly (days). Not enough is known about the mechanism and rate of degradation for individual negatives to say for sure. But given the certainty that the negatives will continue to degrade, important negatives should be duplicated as soon as possible.
- 3. For extremely important negatives which have reached stage 5 or 6 deterioration, it may be decided that the emulsion should be stripped from the degraded film base and either reattached or duplicated onto another sheet of film. This work should be referred to a trained photographic conservator. The process of emulsion stripping is very difficult and expensive, and not always successful. There are two approaches to the emulsion stripping process. The first involves removing the deteriorated base and relaxing the gelatin pellicle. The pellicle is temporarily placed on another plastic support and a duplicate is made from it. The pellicle is removed from the support, dried and returned to the owner intact but unmounted, along with the duplicate. The second method also strips away the old film base but the pellicle is adhered to another piece of film as it dries.

At this point it should be stressed that only the negatives which show signs of serious degradation need be of urgent concern. The problem, while it is growing, presently affects only a small percentage of negative collections in the United States and some collections have no degradation at all. The major tool for proper preservation management of negative collections is frequent and systematic monitoring as described above.

#### **Environmental Factors**

The health hazards associated with working with degrading acetate and nitrate negatives were recently studied by the University of Arizona for the Arizona State Museum. Their report (Appendix D) concludes that symptoms seen in some workers, such as skin irritation, itching, nausea, headache, eye irritation, reddening of the face and chest area, sneezing, rashes, or sores, can be caused by deteriorating film bases, both nitrate and acetate. This occurs primarily due to absorption of irritants through mucous membranes. The levels of harmful products were found to be far below hazardous levels. Any danger to staff can be minimized by reducing both dosage and concentration of the irritants by: 1) wearing gloves when handling negatives; 2) providing an adequate change of air with a fan; and 3) limiting the time that degraded negatives are handled.

## **Further Testing**

A great deal of work can and should be done by qualified conservators and chemists to learn more about the problem of acetate negatives. Much of this work will involve analytical tests of historical

negatives stored under different conditions and representing a variety of film types. This would provide additional information about the degradation mechanism of cellulose acetate film and help shed further light on why certain negatives degrade before others. This analytical data may also provide methods for testing film to determine its stability thus providing curators and archivists with a useful tool to help manage negative collections. This should certainly be a goal of additional laboratory work.

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#### APPENDIX B - NOTCH CODE REFERENCES

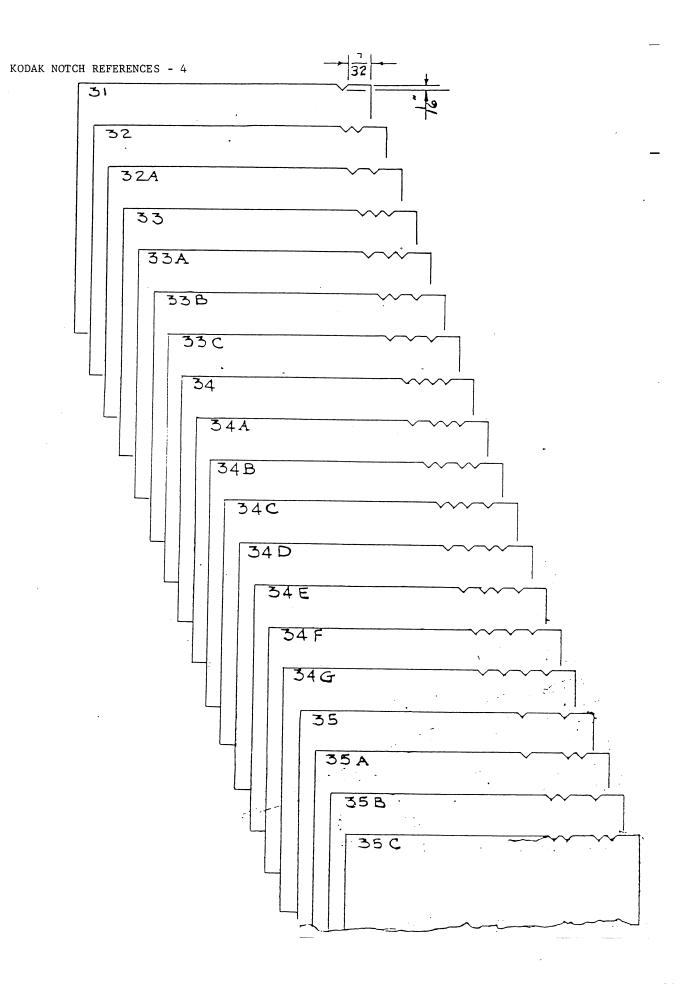
## KODAK NOTCH CODES .....p. 68

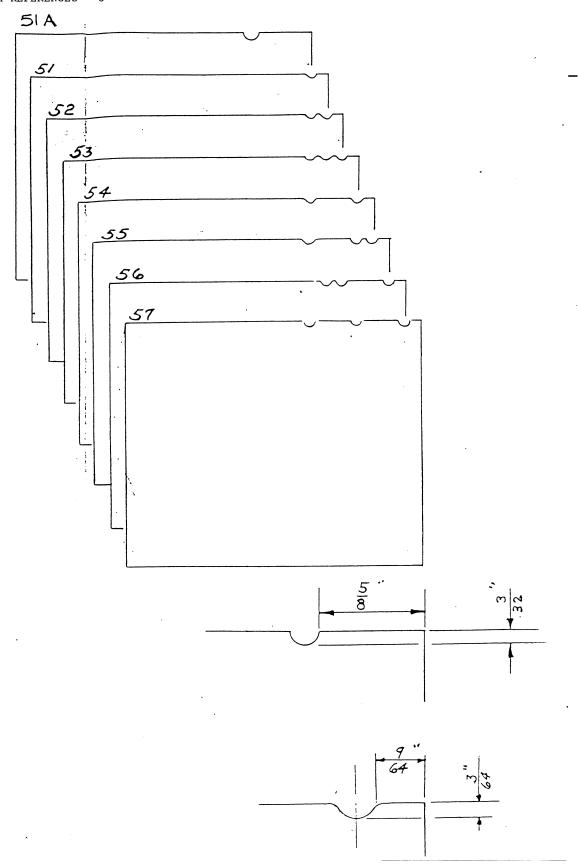
The reference numbers used for Kodak sheet film were received from the Patent Office of the Eastman Kodak Company in Rochester. These references, provided in the following document from Kodak along with the accompanying chronology, provide a very useful history of Kodak film types. The notches accurately represent samples selected for this survey, but the chronology was not consistent with dated negatives found in various collections.

Notch reference #1 (a single square) was used on Kodak's first safety sheet film product, Pan Portrait Film, in 1925. All of Kodak's safety base products from 1925 to about 1949 began with this notch on the far right of a film's notch code, (holding the negative with the emulsion towards you, notch in the top right). Negatives from this period were coded with notch references 1-14B. Pre-1949 Kodak films on nitrate base were always identified with a "V" shaped notch in the first position.

## OTHER MANUFACTURER'S NOTCH REFERENCES ....p. 85

Notch references for Agfa/Ansco, Hammer, Defender, and Dupont Defender are not available from the manufacturers. The numbered references included here were assigned during the course of this project.





## $\frac{\text{HISTORY OF CODE}}{\text{NOTCHES}}$

## NOTCH FILM CODE FILM NAME

1	1101	Par Portrait (1935) Discontd.
	5101	Par Portrait (1938) Discontd.
	7581	Asochrome (1940) Discontd. 1946
	6123	Autopositive Commercial (1942) Discontd.
	6126	Appan (1942) Trans. to 32A (1953)
	6130	
		Infrared (1942) Discontd. 1970
	Exp.	Kodalith Panchro (1942) Discontd. 1949
	6565	Kodagraph Proc. Pan Stripping (1942) Discontd. 1949
	7582	Kotavachrome (1942) Discontd. 1949
	5601	Masking Pan (1942) Discontd. 1947
	5560	Contact Screen (1945) Trans. 1952
	Exp.	Aero Positive Transparency (1946) Discontd. 1949
	5204	Micro-File (1946) Discontd. 1953
	5570	Pan Masking (1946) Discontd. 1967
	5246	Direct Positive Pan (1946)
	7009	Verichrome (1949) Discontd. 1956
	5552	Opalure Print (1949) Trans. to # 9 (1958)
	6574	Aerographic Positive (1949) Discontd. Notching 1953
	6564	Kodalith Pan Stripping (1949) Discontd. 1963
	5211	Linagraph Ortho 1952 Code changed to 5471 (1960)
	5471	Linagraph Ortho (19603 Discontd. 1971
	5214	Linagraph Shellburst (1952) Code changed to 5474 (1959)
	5474	Linagraph Shellburst, Gray Base (1959)
	5244	Linagraph Pan (1952) Code changed to 5479 (1963)
	5365	Fine Grain Dupl. Pos. (1952) Code changed to 5366 (1965)
	6014	Verichrome Pan (1956) Discontd. 1960
	5574	Aerial Positive 1954 Code changed to 5435 (1958)
	5435	Aerial Positive (1958) Discontd. 1967
	6013	Verichrome Pan (1960) Discontd. 1961
	2566	Kodalith Royal Ortho, Estar Base (1960) Discontd. Notch
	5218	High Speed Infrared (1960) Discontd. 1970 1961
	5455	High Contrast Copy (1960) Discontd. 1969
	6041	Verichrome Pan (1961)
	4151	Dye Transfer Receiving Estar Thick Base (1965)
	5480	XR Extended Rnge (1964 Discontd. 1967
	4589	Gravure Resist, Estar Thick Base (1965) Discontd. 1969
	2474	Linagraph Shellburst, Estar Base (196)5
	2475	2475 Recording, Estar Base (1965)
	5028	Ektacolor Slide (1964)
	5256	Ektachrome MS, for Daylight (1965) Changed to "SO" 1971
	5258	Ektachrome ER, Type B (1965) Changed to "SO" 1971
	5459	Micro-File AHU (1965) Discontd. 1969
	2256	Ektachrome MS, Estar Base (1966)
	4588	Projection Print, Estar Thick Base (1966)
	4427	Aerographic Duplicating, Estar Thick Base (1967)
	2448	Ektachrome MS Aerographic, Estar Base (1967)
	2 <del>44</del> 6 2476	Linagraph Shellhurst Estar-AH Rase (1966)

## NOTCH FILM CODE FILM NAME

1 (contd.)	2479 RAR, Estar-AH Base (1966) 24 84 Pan, Estar-AH Base (1967) High Speed Recording, Estar-AH Base 2496 RAR, Estar-AH Base (1967) 2498 2498 RAR, Estar-AH Base (1967) High Speed Ektachrome, Daylight Type High Speed Ektachrome, Type B (1967) 4-X Negative (1967) Ektachrome ER, Daylight (1966) Chngd Super-XX Aerographic (1967) Discontd. Aerographic Duplicating (Estar Base) (1962) Kodak 24 92 RAR Film (Estar Base) (1962) Ektacolor ID/copy 5022 (1971)	(1967) To "SO" 1971 7) To "SO" # 1971 . to "SO" # 1971 . 1968 968)
	'SO" Films and customer orders that require a not #1 notch unless otherwise shown on these sheets.	tch will normally utilize the
2	Super Ortho Portrait (1935 Discontd. Super Ortho Portrait (1935) Discontd. Super Ortho Portrait (1935) Discontd. Super Portrait (1935) Discontd. Super Portrait (1935) Discontd. Super Portrait (1935) Discontd. Portrait Super Speed Matte (1942) Discontd. Super Speed Ortho Portrait (1938) Tra So-131 Pan-X 100 (Estar Thick Base) (1938) Discontd.	ns. to 4C (1949)
2A	Commercial (1935) Discontd. Commercial (1935) Discontd. 194 Commercial (1935) Discontd. 194 Commercial (1935) Discontd. 196 Commercial Thin Base (1942) Discontd. Commercial (Estar Base)(1960) Name & Commercial Estar Thick Base (1964) Commercial (1967)	57 1953
3	Commercial Ortho (1935) Discontd. Commercial Ortho (1935) Discontd. Commercial Ortho (1935) Discontd. Commercial Ortho (1935) Discontd. 1966 LS Pan (Estar Thick Base) (1964) Discont	
3A	Commercial Pan (1935) Discontd. Commercial Pan (1935) Discontd. 1940 Single-Coated X-ray, Green Sensitive (1935) Single-Coated X-ray, Green Sensitive (1935)	

NOTCH	FILM C	ODE FILM NAME	
3B	1106 5106 6111 6562 6111 1961 4111 Discon	Process (1935) Discontd. Process (1935) Discontd. 1940 Contrast Process Ortho (1940) Discontd. 196 Kodagraph Contrast Process Thin Base (194 Wirephoto Process Ortho (1953) Discontd. 1 Contrast Process Ortho (Estar Thick Base) 1 td. 1970 Wirephoto Process Ortho (Estar Thick Base) Contrast Process ORTHO (Estar Thick Base) Process Ortho for WIREPHOTO (Estar Thick	967 967 967 1967 Code changed to:
		Trocess Offilo for WIKEFITOTO (Estai Tille	LK Base) (1970)
3C	1114 2114 5114 6114 2558	Portrait Pan (1935) Discontd. Portrait Pan (1935) Discontd. Portrait Pan (1935 Discontd. Portrait Pan (1935) Trans. to # 34 (1949) Kodalith Pan Processor (Estar Base) (1970)	0)
4	5112 6112 6563 4152	Process Pan (1935) Discontd. 1940 Contrast Process Pan (1940) Trans to # 34 Kodagraph Process Pan (1940) Trans. to Kodagraph C. T. C. (1940) Discontd. 1942 Ortho Scanner (Estar Thick Base) (1967)	
4A	5105 6105	,	
Trans. to	6140 # 35 (193	50)	Panatomic-X (1938)
P.B. (1958		l. 1960	Contrast Process Ortho
Thick Bas	4135 e) (1965) T SO-133	o Frans. to 34G 1968 Gravure Positive (Estar Thick Base) 1967 Tr	Gravure Positive (Estar ans. to 34G 1968
4B	1112 5113 6113	Commercial Matte (1935) Discontd. Commercial Matte (1935) Discontd. 1942 Commercial Matte (1940) Discontd. 1964	
4C	5117 6122 4166	Ortho Press (1935) Discontd. 1942 Super Speed Ortho Portrait (1949) Discontd. Royal-X Pan (Estar Thick Base) (1970)	1967
4D	5554 6554 6573 6573	Kod alith Blue Sensitive (1935) Discontd. Kodalith Blue Sensitive (1935) Discontd. Highlight Masking (1947) Discontd. 1963 Professional Line Copy (1963)	

NOTCH	FILM COI	DE FILM NAME	
4E	5557 6557 6558 6567 8557	Ortho Kodalith (1935) Discontd. 1942 Ortho Kodalith (1942) Discontd. Kodalith Ortho Thin Base( 1942) Trans. to # 9 (1943) Kodalith Half Tone (1942) Discontd. Kodalith Ortho Cartographic (1942) Discontd.	
4F	 6146	Panchro Press Safety (1935) Discontd. 1940 Super Pan Press, Type B (1940) Trans. to # 31 (1949)	
4G	1116 2116 6116 5116 6127 9123 4143	Super Sensitive Pan (1935) Discontd. Super Sensitive Pan (1935) Discontd. Super Sensitive Pan (1935) Discontd. 1940 Super Sensitive Pan (1935) Discontd. 1940 Super Panchro Press Sports Type (1946) Trans. to # 35 Commercial P.B. (1957) Discontd. 1961 High Speed Infrared 4143 (Estar Thick Base) (1970) SO	(19
8	6559	T.B. Stripping (1935) Discontd. 1964	
9	5109 5118 5120 5121 6129 6129 6136 6527 6139 5301 5552 5561 5574 6555 5159 6558 7302 7303 5552 4139 4527 4514 SO-183	Transmission, Type A (1942) Discontd. 1961 Blue Base X-ray (1942) Discontd. Blue Base X-ray (1942) Discontd. Blue Base X-ray (1942) Discontd. Wirephoto Super Speed (1942) Changed name to: Wirephoto, Type C (1953) Discontd. 1967 Single-Coated X-ray, Blue Sensitive 1942 Changed To: Single-Coated X-ray, Blue Sensitive 1958 Discontd. 1967 Transmission, Type C (1942) Discontd. 1967 Positive (1942) Discontd. 1949 Kotava (1942) Discontd. Translite Matte (1942) Discontd. White Topographic (1942) Discontd. Kodalith Process Screen Thin Base (1942) Discontd. Industrial X-ray, Type M (1942) Discontd. Kodalith Ortho, Thin Base (1942) Discontd. Fine Grain Positive (1949) Code changed to: Fine Grain Positive (1965) Reverted to Code 7302 (1965 Opalure Print (1958) Kodak Transmission, Type C (Estar Thick Base) (1967) Single-Coated X-ray, Blue Sensitive Estar Base (1967) Kodak RP/D X-OMAT Radiograph Dupl. (1970) Scanner Pan Film (ESTAR Thick Base) (1969) ( to #1 not 1g) 1970	
12	6128	Super Panchro Press (1938) Discontd.	
	Pa	nchro Press Super-X (1942) Discontd.	
	2133	Separation Neg. Type II (Estar Base) (1960) Code & Name changed to:	
	4133	Separation Neg., Type II (Estar Thick Base) (1964)	

NOTCH	FILM C	CODE FILM NAME
12A	5133	No-Screen X-ray (1938) Discontd.
	6137	Kodacchrome Daylight Trans. to # 14 (1938)
	1510	Nitrate Matrix (1949) Discontd. 1951
	4509	RP/SU X-0mat Subtraction (1970)
13	2131 S	Kodachrome, Type B (1938) Trans, to # 56 (1949) Spearation Neg. P.B. (1957) Discontd. 1961 Separation Neg. Type I (Estar Base) (1960) Code & Name changed to: Separation Neg., Type I (Estar Thick Base) (1964)
13A	6147	Super Ortho Press (1938) Discontd. 1956
	6147	Plus-X Pan (1961) Discontd. 1964
	4147	Plus-X Pan (Estar Thick Base) (1964) Name changed to:
	4147	Plus-X Pan Professional (Estar Thick Base) (1967)
13B	6125	Eastman Safety Gravure (1938) Discontd.
	2134	33 Positive (Estar Base) (1960) Code & Name changed to
	4134	33 Positive (Estar Thick Base) (1964) Discontd. 1965
13C	6145 2138	Ortho-X (1938) Discontd. 1956 Tri-X (Estar Base) (1960 Code & Name changed to:
	4138	RS Pan Estar Thick Base (1965) Discontd. 1970
	6138	RS Pan (1960) Discontd. 1965
14	6137	Kodachrome, Daylight (1938) Trans. to # 54 (1949)
	6523	Single-Coated X-ray, Green Sensitive, Type 0 (1959) Discontd. 1962
14A	6143	Tri-X (1938) Trans to # 33 (1950)
	6125	Gravure Copy (1958) Name changed 1969
	6125	Professional Copy (1969) Discontd. 1970
	4125	Professional Copy (Estar Thick Base) (1970)
14B	6142	Super-XX (1938) Trans. to # 32 (1950)
	6144	Royal Ortho (1956) Discontd. 1965

	4163	Tri-X Ortho (Estar Thick Base) (1965)
14C	6148	Kodatron (1940) Discontd.
	5510	Matrix (1946) Code changed to:
	5150	Matrix R959l Discontd. 1960
	6137	Kodachrome, Daylight - Trans. to .# 14
	1150	Matrix (Estar Base) (1960) Code & Name changed to:
	4150	Matrix (Estar Thick Base) (1964)
KODAK NOTCH REFERENCES - 13		
NOTCH	FILM CO	ODE FILM NAME
14D	6568	Kodagraph Commercial Screen (1941) Discontd.
	6138	Kodachrome, Type B - Trans. to # 13
	5513	Flexichrome Stripping 1949 Code changed to:
	5151	Flexichrome Stripping (1959) Discontd. 1961
14E	9570	Pan Masking P. B. (1958) Discontd. 1960
	1570	Pan Masking Estar Base) (1960) Code & Name changed to:
	4570	Pan Masking Hstar Thick Base) (1964)
14F		
14G		
22		
22A		
23		

23A

23B

23C

24

24A

24B

24C

24D

24E

24F

NOTCH NAME	FILM CO	DDE FILM
24 G		
31	5160	Industrial X-ray Type A (1942) Discontd.
	1009	Verichrome (1942) Discontd.
	2009	Verichrome (1946) Discontd.
	1515	Wash-Off Relief (1942) Discontd.
	1510	Matrix (1946) Trans. to r# 12A (1949)
	6146	Super Pan Press, Type B (1949)
32	5135	Industrial X-ray, Type K (1942) Discontd.
	6142	Super-XX (1950) Discontd. 1965
	4142	Super-XX Pan (Estar Thick Base) (1965)
32A	6141	Royal Pan (1953) Discontd. 1965
	6126	Appan (1953) Discontd. 1958
	4141	Royal Pan (Estar Thick Base) (1964)
33	5134 6143	Industrial X-ray, Type F (1942) Discontd. Tri-X Pan (1950) Discontd. 1961
	4164	Tri-X Pan (Estar Thick Base) (1963) Name changed to:
	4164	Tri-X Pan Professional (Estar Thick Base) (1967)
33A	5141	Fine Grain X-ray (1942) Discontd.
	SO-191	Polycontrast Print (ESTAR Thick Base) 1971
33B	6562	Kodalith Pan (1942) Discontd. 1960
	2568	Kodalith Pan (Estar Base) (1960)

33C	5120	Blue Base X-ray (1942) Discontd.
	1511	Pan Matrix (1946) Discontd. 1949
	5511	Pan Matrix (1946) Code changed to:
	5149	Pan Matrix (1957) Discontd. 1964
	1149	Pan Matrix (Estar Base) (1960) Code & Name changed to:
	4149	Pan Matrix (Estar Thick Base) (1964)
34	6614	Portrait Pan (1949) Discontd. 1969
34A		
34B	6112	Contrast Process Pan (1950) Discontd. 1970
	6563	Kodaline Process Pan (1949) Discontd. 1950
	4153	Contrast Process Panchromatic (Estar Thick Base) (1970)

34C

# KODAK NOTCH REFERENCES - 15

NOTCH	FI	LM CODE	FILM NAME
34D			
34E			
34F			
34G	5512	Pan Matrix Reversal (19	947) Discontd. 1954

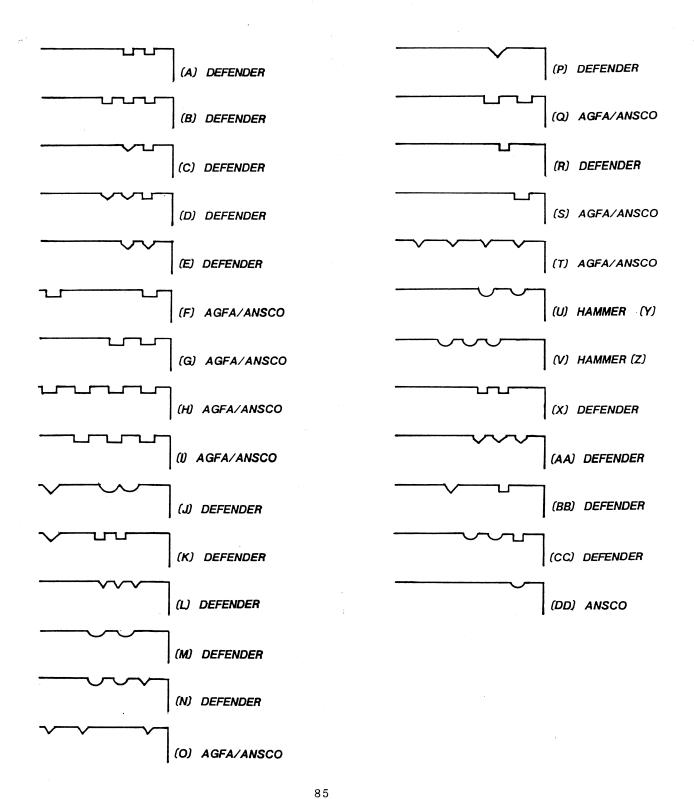
	SO-133	Gravure Positive (Estar Thick Base) (1968) Discontd. 196_
	4135	Gravure Positive 4135 (Estar Thick Base) (1968)
35	6140	Panatomic-X (1950) Discontd. 1969
35A	6127	Super Pan Press, Sports Type (1949) Discontd. 1953
	612	8 Royal,-X Pan (1957) Discontd. 1965
	412	8 Royal-X Pan 4128 (Estar Thick Base) (1965) Discontd. 1969
35B		
35C		
41		
42		
43		
44		
45		
46		
<del>-</del> 1	C101	
51		Ektachrome Daylight (1946) Trans. to # 61 (1957)
		Recordak Micro-File Card (1970)
	2950	Recordak Diazo TM Film 2950 (ESTAR Base) 1970
	2950	Recordak Diazo M Film 2950 (ESTAR Base) 1969
	4950	Recordak Diazo M Film 4950 (ESTAR Thick Base) (1969)
	4950	Recordak Diazo TM Film 4950 (ESTAR Thick Base) 1970
	SO-404	Recordak High Speed Diazo (ESTAR Thick Base) 50-404 Disc. 1972

	NOTCH	FILM CODE FILM NAME
	51A	Single-Coated, Green Sensitive, Type 0 (1963) Discontd. 1966
		4523 Single-Coated, Green Sensitive, Type 0 (Estar Base) (196_)
		Name changed 1969
		4523 Single-Coated, Green Sensitive 1969
		SO-363 Single-Coated, Green Sensitive, Type I (Estar Base)(196_) Discontd. 1968
	52	6102 Ektachrome, Type B (1946) Trans. to # 62 (1957)
	53	6104 Ektacolor, Type B (1946) Trans. to # 64 (1957)
	54	Kodachrome, Daylight (1949) Discontd. 1951
		6103 Ektacolor, Type S (1956) Trans. to T 63 (1957)
56		Kodachrome, Type B (1949) Discontd. 1951
57		Ektacolor Print (1949) Trans. to # 65 (1957)
58		
59		
60		
61	6101	Ektachrome, Daylight (1957) Discontd. 1960
62	6102	Ektachrome, Type B (1957) Discontd. 1960
63	6103	Ektacolor, Type S (1957) Code & Name changed to:
	6101	Ektacolor Professional, Type S (1963)

- 64 6104 Ektacolor, Type B (1957) Discontd. 1958
  - 6106 Ektacolor, Type L, (1959) Code & Name changed to:
  - 6102 Ektacolor Professional, Type L (1964)

	NOTCH	FILM	CODE FILM NAME
	65	6105 E	Ektacolor Print (1957) Discontd. 1959
		4106 N	Vericolor Professional, Type L (Estar Thick Base) (197_)
	65A	4105	Vericolor Professional, Type S (Estar Thick Base) (197_)
	66	6106	Ektacolor, Type L (1957) Trans. to # 64 (1959)
	67	6115	Ektachrome, Daylight Type (1958)
	68	6116	Ektachrome, Type B (1958)
	69	6108	Ektacolor Print (1958) Code changed to:
		6109	Ektacolor Print (1962) Discontd. 1972
		4109	Kodak Ektacolor Print (1971)
	70	6110	Ektacolor Internegative (1959)
	71	2104	Tri-Mask (Estar Base) (1961) Code & Name changed to:
		4104	Tri-Mask, (Estar Thick Base) (1964)
	72	6119	Ektachrome Duplicating (1966) Discontd. 1971
	73	6120	Ektachrome Duplicating (1971)
NOTE:	Approval Ca	ard # 5068	8 changes Notches - 1949-1950

## BORDER NOTCH IDENTIFICATION OF VARIOUS FILM TYPES



#### APPENDIX C - BIBLIOGRAPHY

For the purpose of this report, bibliographic items were selected to provide a cross section of useful information relating to the manufacture, history, and aging of cellulose ester film negatives. Highly technical sources have not been included.

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American National Standards Institute. The following titles may be purchased by writing to the Institute, Sales Department, 1430 Broadway, New York, NY 10018:

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#### APPENDIX D - HEALTH CONCERNS

Date: September 10, 1985 MEMORANDUM

University of Arizona
Dept: Risk Management

To: George Sample, Arizona State Museum

From: Steve Holland, Safety Officer

[Signature] Campus Ext 1-1590

Subject: Final Report - Environmental survey of the

photographic negative storage and sorting area

Enclosed is the summary report of the findings from air sampling performed in the nitrate and di-acetate negative storage and sorting area. As the report indicates, the air sampling results are not entirely conclusive. However, the recommendations are based upon prudent industrial to hygiene practice for the control of air contaminants as well as the existing design of the ventilation system.

If you have any questions or comments, please call me at 1-1590.

cc: Martha Anderson

Patricia Weyermann Hollinshead

Dr. Mark VanErt

## ARIZONA STATE MUSEUM PHOTOGRAPHY COLLECTION

## ENVIRONMENTAL SURVEY REPORT RISKMANAGEMENT DEPARTMENT STEVEN C. HOLLAND

## Description of the Problem

The Arizona State Museum has a collection of aged nitrate and diacetate photographic negatives which have been in the process of being sorted, cataloged, and duplicated by museum employees. During the handling process, at least two employees have experienced a variety of health problems believed to be associated with exposure to the negatives. These health complaints have included skin and eye irritation, headache, nausea, and difficulty in breathing. The symptoms described above are most frequently evident following an exposure of several hours or more. In addition to eye irritation, one employee experienced a perceived swelling of the eye accompanied by permanent discoloration of a pair of contact lenses. The other affected employee has developed an increased sensitivity to the negative materials, feeling the onset of symptoms after even a brief exposure.

### **Initial Monitoring Results**

During the initial visits to the work areas involved, several potential contaminants were considered to have a good possibility of contributing to the problems. Oxides of nitrogen were considered as these are generated during the deterioration of cellulose nitrate in air. Sensitive air sampling for nitrogen oxides was performed at the work table and under the plastic sheeting where negatives were stored. The concentration in the room was non-detectable, however, the concentration under the plastic sheeting was approximately 2 parts per million (ppm) of nitrogen dioxide. Silver salts from the negative emulsion were also considered as a possible skin irritant. Filter sampling for silver salts indicated a non-detectable level of this contaminant. Dr. Mark VanErt of the School of Health Related Professions became involved in the study and found that the diacetate negatives were off-gassing acetic acid. Several negatives sealed in a flask for three days generated a concentration of acetic acid at 60 ppm within the flask.

## **Recent Monitoring Results**

Detailed air monitoring was conducted by Steve Holland and Dr. VanErt on June 4, and June 13, 1985. On .the first day, the museum worker (Pat Weyermann Hollinshead) handled nitrate negatives exclusively. On the second sampling day, only diacetate negatives were handled. Seven air samples were collected on each day. Sampled locations were in the worker's breathing zone, in the immediate desk work area and throughout the room. This room is presently used almost exclusively for negative storage and sorting. After completing the second day of sampling, it was noticed that upon peeling the emulsion away from the backing of a discarded di-acetate negative, a strong organic odor was immediately evident as well as some dampness between these layers. Several such negatives were peeled and sealed in a flask to contain vapors as they were release. After three days, an air sample was collected from inside the flask and analyzed using gas chromatography/mass spectroscopy to identify all organic compounds present. The results of this test indicated acetone and mesityl oxide in a relative ratio of approximately five to one. Based on this information, the previously collected air samples were split, analyzing two for mesityl oxide and acetone while the remainder were analyzed for acetic acid. The samples analyzed for mesityl oxide and acetone were from the immediate area of negative handling.

Analytical results from these samples indicated non-detectable concentrations of all three contaminants. Detection limits are on the attached analytical report.

#### Conclusions

Although air monitoring to date has shown non-detectable levels of contaminants in the breathing zone, the symptoms experienced by the workers are significant enough to strongly indicate the presence of an air contaminant or combination of contaminants, presumably at a very low concentration. The compounds which have been identified as being present are nitrogen dioxide, acetic acid, acetone, and mesityl oxide. All of the varied symptoms reported can be associated with at least one of these in the published industrial hygiene literature. Even at very low concentrations, synergistic effects may be occurring where two or more compounds act-together to aggravate a symptom. The important conclusion then, is that although no individual is being overexposed to any of the listed chemicals according to industrial standards, the very low exposure which does exist is sufficient to be the most probable contributing factor to the health problems experienced by the photography collection workers.

#### Recommendations

The symptoms being experienced by the photography collection staff are almost certainly dose-related, even at very low concentrations. Dose is a function of time of exposure and concentration. By reducing both of these, symptoms should decrease as well. Although contaminant concentrations are very low, they can be lowered even further with some minor ventilation improvements. The negative storage room, when built, enclosed a large return air vent for the museum.. building's air conditioning system. The room is at strong negative pressure relative to the exhibit hall with air entering only through a small vent located at ceiling height on the west end of the room. When the door is open, a much greater quantity of air moves through the room, thereby diluting any existing air contaminants to a lower concentration. If the door needs to be closed for privacy or security needs, then the door should be codified to install an air grille, allowing more air to ventilate into the room at all times. In addition to this modification, the actual negative storage area should be relocated directly beneath the return air grille. Visual observations using smoke candles indicate a higher room air velocity in this region due to the movement of air into the return air duct. This increased velocity and overall level of air movement will further aid in diluting air contaminants. These ventilation and location changes will result in a positive improvement in the dilution of air contaminants. However, since the symptoms which have been reported were al: present at very low concentrations, the time of exposure may also require modification. The amount of time spent working with the negative collection will have to be determined subjectively by those working with it. Even with improvements in ventilation, marathon work sessions of several hours or more should be avoided if possible. A reasonable time limit of exposure might be two or three hours, but the worker must make this decision based on the presence or absence of symptoms. By taking precautions of not working too long with the negatives and ensuring good air flow into the room, it should be possible to continue the project without adverse health effects. If this proves not to be the case and symptoms persist, even after very brief exposures, then more sophisticated alternatives will need to be investigated in the area of exposure control and work process modification.