NPIC/TDS/D-666-67
1 February 1967

MEMORANDUM FOR THE RECORD

SUBJECT: Photobleach Photography; Evaluation of Final Report Phase II

1. Photobleach studies, Phase II, was entered into with the [redacted] 25X1 [redacted] on 15 June 1965 for the purpose of extending the fundamental work on the reaction mechanism of the photobleach process initiated in Phase I the previous year. Other goals of Phase II were:

a. To continue studies of the relationship between the photographic properties and the operating variables to obtain use information of the material.

b. Formulation of suitable dyes and test films.

c. Demonstrate the feasibility of achieving the objectives established at the outset of Phase I.

2. The objectives established for this development under Phase I are as follows:

a. A black and white (or colorless) film, with D_{max} of 3.0 or more over the visible region, and a D_{min} of 0.05 or less.

b. A resolution capability of 400 line pairs/mm.

c. Speed equivalent to ASA 0.1.

d. Ability to control the H&D curve from gamma 0.8 to 2.5.

e. Stable storage of material, both before and after exposure for at least one year.

3. Early in Phase II it became obvious that several of the objectives, such as speed and D_{max}, would not be achieved. There did however, appear to be a good possibility of achieving a photobleach material of lesser speed and maximum density. Therefore the effort was re-oriented toward a set of interim objectives of:

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a. D max of at least 2.0 and a D min of 0.10.

b. Resolution of at least 200 line pairs/mm.

c. Latitude of 11 steps of a 0.15 gradiation density step wedge.

d. Control of gamma from 1 to 2.

e. Storage for one year before exposure and six months after exposure, and

f. Speed sufficient to expose a 4 x 5 inch sheet in no more than 30 seconds.

4. Much of the first six months of Phase II was spent experimenting with various dye combinations in an effort to obtain a material having good D min and D max characteristics and capable of being heat locked to prevent deterioration. Section III of the report (Alternate systems) deals with many experiments that were made concerning such matters as; photosensitive agents, dyes, additives, polymers, and heat locking. It was not until October 1966 that a formulation, "TMI", (Trimethylindoaniline) in combination with iodoform suspended in an alcohol butrate polymer (ASB), was produced that exhibited the desirable characteristics of density, speed, latitude and locking, or keeping qualities. Therefore most of the report is devoted to extolling the qualities and possibilities of this material.

5. Much progress has been made toward meeting the above interim objectives, as shown in exhibits contained in the report, figures, 1a, 1b, 2a, 2b, and 4:

a. Figure 1a is a film sample of the photobleach material and, except for the blue color, is a fairly faithful reproduction of the original, which is shown by comparing figures 2a and 2b one of which (2b) is made from the silver halide original the other (2a) is made from the photobleach film figure 1a.

b. Figure 1b represents an initial attempt to coat paper with photobleach. It is not very good, as of now, but does indicate possibilities in this direction.

c. The resolution possibilities of the photobleach film are shown in figure 4 which resolves about 200 lines/mm.

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d. Since the writing of the report, reproductions of a gray scale have been received (the reproduction and the step wedge from which it was made are included with figure 1a). When viewed with light passed by a series OA (yellow-green) filter, it shows a latitude of about 14 shades of gray. Also, from observation of this strip under filtered light, it is reasonable to accept the D_{min} and D_{max} figures of 0.1 and 2.0 respectively as stated in the report as having been achived.

e. The heat development technique discussed in the report has provided a reasonable storage capability and the samples supplied with the report will not fade when exposed to white light. However, the development time of two minutes far exceeds the desired time of 30 seconds for each print. It is interesting to note, however, that the film is relatively insenstive to all but ultra-violet light, which is used for exposing.

f. The report shows little or no effort toward gamma control; however, the report does state that with the application of heat during the exposure there was an observed shifting of the slope of the H&D curves. The means for controlling this shift and the lower and upper limits of gamma are not presently known.

6. The recommendations for further work on photobleach cover such matters as:

a. Optimization of the latest film formulation.

b. Standardization of operational procedures.

c. Extend the investigation of contrast or gamma control.

d. Develop appropriate packaging for the sensitized material.

7. Inasmuch as the contract on this project has been terminated no action on these recommendations will be taken at this time. However, because of the great progress made on photobleach during the last few months of the contract, further investigation should be made at some future date.

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8. Because of the great difficulty anticipated in developing a black photobleach film, further effort in this direction is not recommended at this time. 25X

[redacted]

Support Systems Branch, TDS/DS, NPIC

Attachment:
Final Report on Photobleach Photography Phase II

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SUBJECT: Photoflash Photo. Eval. Final Report Phase II

ORIGINATOR [redacted] DATE: 30 Jan. 67

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COMMENTS: ?

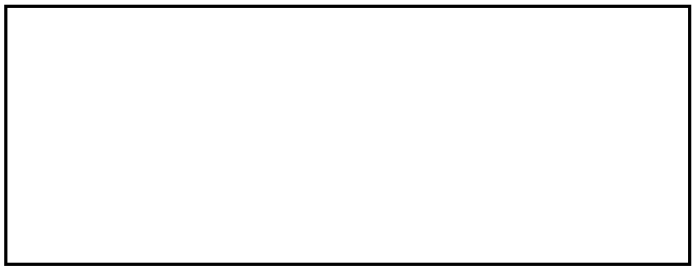
Concur w/recommendations in para 8. plus other reservations 3 Feb 67.

FINAL REPORT

Photobleach Photography

Phase II

30 November 1966



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FIGURES

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ABSTRACT

The progress made in the second year's effort in the development of the Photobleach Photography process is described. A blue film has been developed which bleaches to a clear neutral, and is developed and fixed by a short heat treatment. This film, which satisfies most of the requirements for a photocopy material, is described in detail. A sample of the film is attached, as Figure 1.

The work leading to the development of the above film is described. Several photosensitive agents have been evaluated, including chlorine-containing polymers. Many dyes have been screened. Dyes which do not complex with, and transfer energy to the photosensitive agent have advantages in more rapid heat fixing. Several additives have been tested for increase in photosensitivity of the photobleach system. One additive appears promising. The chemical nature of the polymer film has been found to markedly affect the sensitivity of the film.

The mechanism of the photobleach reaction is ascribed to the photolytic formation of acid which reacts with the dye, thus bleaching it. A new process is described in which photolytic formation of base similarly bleaches some dyes.

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I. INTRODUCTION

Photobleach Photography is in its present form a system for the reproduction of monochrome direct positive copies of transparencies. The system is dry, rapid, and has high resolution. In brief, the system consists of a polymer film, containing a bleachable dye and a photosensitive agent, cast on a suitable support, such as Mylar, glass or paper. Light passing through the portions of the transparency with low optical density causes a reaction to take place in the photobleach film which results in the bleaching of the dye. In some cases the bleaching takes place immediately, in others a post-exposure heat treatment speeds up the reaction. The heat treatment also fixes the film so that it is no longer sensitive to light.

This process has been under investigation in these laboratories for the past two years. The results of the first year's work have been described in a final report, "Black and White Films", which describes in detail the apparatus and techniques employed in the study. These descriptions will not be repeated in this report.

This report will describe the results of the second year's effort (labeled Phase II) of the Photobleach Photography project. During the year, work has proceeded on a large variety of dyes and systems. Toward the end of the year, a film was developed which shows most of the desired properties in a photocopy system. Since this film is likely to be of the greatest interest, it is described in detail in Section II. The properties which have been sought, and the degree to which the film achieves them are detailed. In Section III, the work on other film systems, which have proven to be less successful, is described. This effort included screening of new materials, evaluation of modification of the process and of new processes, and further exploration of the mechanism of the reactions involved in the process. Recommendations for further work are summarized in Section IV.

II. OBJECTIVES AND STATUS

A. Objectives

The objectives of the Photobleach Photography program are defined in terms of the properties of the photocopy material to be developed in the course of the program. Two sets of objectives exist: first, the properties to be desired ultimately in a material after a continued development effort, and second, the properties desired in a material that can find immediate application, developed as the result of the current year's work. The second set of objectives, which are of immediate concern, are as follows:

1. Density: A black starting material with D_{max} at least 2.0, which bleaches to a material with a fairly uniform absorption in the visible region with a neutral color and a D_{min} of 0.10 or less.

2. Sensitivity: Sufficient to permit a demonstrated capability of producing a 4 x 5 contact print with an exposure of not more than 30 seconds, using a light source of less than 1100 watts power.

3. Resolution: 200 lines/mm.

4. Latitude: 11 steps of a 21 step tablet.

5. Storage capability: One year before exposure, six months after exposure.

6. Gamma control: In the region from 1 to 2.

To put these objectives into historical perspective, the proposal for the program under review was written in terms of more stringent requirements for density, sensitivity, and resolution, but did not predict that these requirements would all be met in a single material. It stated further that work on contrast control would be deferred to a Phase III program, as would the attempt to derive a single photocopy material having all the required properties. The objectives listed above were later agreed upon, in January 1966.

B. Present Status

In this section, the properties of the available formulation which best meets the requirements for a photocopy material will be dscribed. This formulation was first tested in October 1966, and has not been optimized as to relative proportions of the several component materials. Nevertheless, it meets all the requirements listed above except for D_{max} and for the range of contrast control. This formulation (hereinafter "the TMI film") consists of a

single dye, TMI (N, N, 2-trimethylindoaniline), the photosensitive agent iodoform, in Eastman alcohol soluble butyrate polymer (ASB) on a Mylar, glass or paper substrate. On the premise that a sample is worth a page of description, examples of contact copies on Mylar and on paper of a positive transparency aerial photograph are shown as Figure 1. Figure 2 shows enlargements of photographs taken of the original positive used to make Figure 1, and of the copy made on TMI film, photographed through a yellow filter.

Another dye, DEMI (N, N diethyl-2-methylindoaniline) gave preliminary results similar to those of TMI, but has not been tested as extensively. The following discussion applies specifically to the TMI film. It is probable that DEMI films would give results differing only in minor details from the TMI results.

1. Density. As can be seen from the example in Figure 1, the material is a deep blue, bleaching to a clear transparent neutral tone. Figure 3 shows the absorption spectrum of a typical film both before and after exposure and development. The optical density is 2 or greater for the film depicted over the wavelength range of 5500-6300 A. Thicker films have been made, having considerably greater optical density, and Figure 3 should not be considered to represent the maximum or even the optimum optical density. For the film depicted, the optical density of the bleached film less than 0.1 at wavelengths above 5700 A, rises slowly to 0.2 at 5000 A, and more rapidly at lower wavelengths. The dashed line in Figure 3 is the absorption spectrum of a Wratten #16 filter which is yellow. When viewed through this filter, the TMI film appears black and yellow rather than blue and clear.

A thicker film, or one with a higher dye concentration, will have a greater optical density, and the bleached film will also have an increased optical density in proportion. Thus, if the optical density at 6000 A is increased from 2.5 to 4.0, the density of the bleached film will be increased from 0.10 to 0.16, and the density range will increase from 2.4 to 3.8. Comparing the absorption curve for the yellow filter with that of the photobleach product at low wavelength, it is apparent that a rather large increase in the amount of bleached product would be needed to materially affect the color produced by it.

2. Sensitivity. The TMI film is sensitive primarily to light at wavelengths of about 4000 A and below. It is not at all sensitive at wavelengths above 5000 A. For these reasons, the most effective illumination is a mercury lamp with a relatively high output in the 3660 A band. We have used a [redacted] 400 watt mercury lamp with a built-in reflector for exposure. At a distance of 20 cm, exposures of 3 to 15 seconds have produced acceptable results, when followed by oven development of eight minutes at 100°C. When the distance is increased to 40 cm, the times are increased to 10 to 40 seconds. The particular light source used in our laboratory is not

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sufficiently uniform to give consistent results over the area of a 4 x 5" photocopy at the shorter lamp to copy distance. In this sense, the photographic quality is better at the greater distance. There is no fundamental reason, however, to prohibit the manufacture and use of a 400 watt lamp which will give flat field illumination at relatively short distances, and thus permit short exposure times. In any event, the sensitivity is well within the stated specifications.

Heat development is needed to bring out the picture with this system. Very little experimentation has been done with time or temperature. In one trial, heating for two minutes at 120°C produced good development. The time can probably be decreased further by raising the temperature. We have no data as yet, however, on the effect of higher temperatures on the dimensional stability of Mylar.

3. Resolution. A photomicrograph of a copy of a resolution chart which gives 226 line pairs/mm on TMI film is shown in Figure 4; 204 line pairs/mm were resolved in this photomicrograph.

4. Latitude. The TMI film has shown as many as 13 steps of a 21 step tablet (0.15 optical density steps), although 11 is more usual. The latitude therefore appears to be adequate to the requirements.

5. Storage. There has not been enough time to evaluate the storage stability of the material. Unexposed material loses its sensitivity over a period of a day or two if left open to the atmosphere. When properly packaged, however, sensitivity has been maintained for a month, which was the period available for the test. There seems to be no reason to believe that sensitivity of properly packaged materials will not be maintained indefinitely.

Exposed and developed films have been exposed in a 400 watt projector for over 20 minutes with no noticeable fading. Such films left in the open in the laboratory for a month have shown no signs of deterioration. It is expected that the films will be stable indefinitely under normal storage conditions, such as are used for color transparencies.

6. Gamma control. No specific work on gamma control of the TMI film has been done. It is expected that gamma can be controlled by control of the development heating period, the exposure, or both, but since no data is available, no definitive statements can be made.

III. ALTERNATE SYSTEMS

This section of the report will summarize the work on systems other than the TMI film described in Section II. Several of these have interesting properties, although none have been as successful as TMI in fulfilling the requirements for a photocopy material. Work has been done in several areas, including screening of dyes, polymers, and photosensitive agents, extensive studies on particular dye systems, effects of external parameters on photographic properties, and mechanism studies. These will be briefly summarized.

A. Screening Experiments

1. Photosensitive agents. The first photosensitive agent used in the Photobleach Process was iodoform. During the course of the project many other photosensitive agents were evaluated in order to find one with superior properties. The main objection to iodoform is that it causes a yellow-brown color to develop in the bleached areas of most systems, due to extensive exposure. In those systems which are sufficiently fast, photographically, the dark color does not develop. It follows, therefore, that the color is probably due to a photodecomposition product of iodoform which is not necessarily related to the dye bleaching reactions. Bromine and chlorine compounds were expected to form products with considerably less absorption in the visible. This has been found to be correct. The bromine and chlorine compounds generally require exposure further into the ultraviolet than does iodoform, however, and are also generally considerably more toxic. Iodoform itself is relatively non-toxic -- it is used medicinally both internally and externally.

The photosensitive halogen compounds which have been tested during the year include:

hexachlorocyclopentadiene
hexachlorethane
carbon tetrabromide
pentabromoethane
tetraiodoethylene
polyvinylchloride
polyvinylidenechloride
2, 3-bis(bromomethyl)-1, 4-dibromobutene-2

Hexachlorocyclopentadiene is an interesting photosensitive agent in that it has no absorption in the visible, does not form products absorbing in the visible, and is reasonably efficient. It has the disadvantage, at least with some dyes, of spontaneously reversing the bleaching process on standing at room temperature, in a period ranging from hours to days. Heat locking is not needed for this agent when used with the class of dyes that do not transfer energy.

Polyvinylchloride and polyvinylidenechloride are polymers used in making films, the latter being sold commercially as Saran. When illuminated with ultraviolet, the films act as photosensitive agents, bleaching dissolved dyes. The polyvinylidenechloride is the more sensitive of the two polymers. With these materials heat fixing is not possible, and the dyes used must be those that do not transfer energy. In addition, cases of spontaneous reversal have been noted, although no effort has been made to determine whether such reversal is a general phenomenon with these films.

The other photosensitive agents tested did not exhibit any pronounced superiority over iodoform, and with the exception of carbon tetrabromide, were not extensively evaluated. Carbon tetrabromide had been used in the first year's program, and also saw considerable use during Phase II, as in many cases it did not form the tan reaction products as extensively as iodoform.

2. Dyes. Screening of dyes proceeded throughout the project. In January, the dye Rose Bengal together with iodoform in the polymer RJ-100 was shown to be more sensitive than any preceding system. Dyes closely related to Rose Bengal, that is, iodinated or brominated derivatives of fluorescein, were shown to be similarly sensitive in the same environment. These dyes were red, all having absorption peaks in the 5200-5600 A region. Bleaching was rapid and clean, with the formation of a clear product of neutral density.

In order to produce a black mixture, dyes are needed whose absorption covers the visible spectrum. Rose Bengal and related dyes cover the central portion of the visible region, and promising yellow dyes were known for the short wavelength region. The known blue dyes, however, were all too slow, and several of the best dyes bleached to colors other than neutral gray. The main screening effort was made for the blue dyes. A search was instituted for green dyes also, but very few green dyes with reasonable bleaching properties were found.

The blue dye with the greatest apparent promise for a black mixture was pinacyanole. This dye is in the cyanine class. It gives a good blue color in films, bleaches to a clear film, and is relatively fast. A black film with good photographic properties was developed from pinacyanole, together with Rose Bengal and p-amino-benzilidenerhodanine. This film, however, proved impossible to heat lock. Despite early experiments indicating light stability, pinacyanole was later found to be insufficiently stable to be used in a film.

Several other blue cyanine dyes were extensively investigated, but none were found to have all the essential properties simultaneously. Some were found to be essentially insoluble in all the polymers being used. Others formed a complex with the photosensitive agents with a much paler color than the original dye. Some were not stable to light.

A green dye, Bindschedler's Green, was found to have excellent photosensitivity in solution. It was not found possible, however, to cast a film in which the dye maintained its color, or showed photobleaching properties. The structure of the dye is related to that of Indophenol Blue, one of the earliest dyes utilized in the photobleach system. Since the solution photosensitivity of the Bindschedler's Green was so great, and since the Indophenol Blue gave good, although slow, blue films, a thorough search was instituted for other dyes of related structure. None were found to be commercially available. A literature search revealed that a few similar dyes had been synthesized in the past. Two of these were selected, and were custom synthesized by Eastman Kodak for us. These are the dyes, TMI and DEMI, described in Section II.

The dyes, TMI and DEMI, although they exhibit the interesting properties described in Section II, are not suitable for mixtures with Rose Bengal. The dyes develop on heating, and are thus faster than Rose Bengal. In addition, there is evidence that Rose Bengal transfers energy to the other dyes. This was demonstrated with mixtures of Rose Bengal and Indophenol Blue in which the Rose Bengal bleaches more slowly than if alone, and the Indophenol Blue more rapidly. A multilayer film might avoid the latter problem, but would introduce other undesirable attributes, such as thicker films and hence lower resolution, and greater difficulty in heat locking.

3. Additives. Several additives were tested during the program to determine if they had any positive effect on photosensitivity. These included:

N-vinyl pyrrolidone
allyl alcohol
9-vinyl carbazole
1-allyl-2-thiourea
anethole

Of these, N-vinyl pyrrolidone showed a variable effect on the bleaching rate of some dyes in polyvinylpyrrolidone films, as high as a factor of 1.5 to 2, and no effect with other dyes. The other additives showed no effect, except for the allyl thiourea, which killed the bleaching reaction.

4. Polymers. Several experiments comparing rates of bleaching of similar systems in a variety of polymers showed no effect of polymer on bleaching rate. In December, a new polymer, RJ-100, a copolymer of vinyl alcohol and styrene, was investigated, and showed an increase in bleaching rate of a factor of four or more with some dyes and no effect with others. Dyes which were particularly improved included Rose Bengal and Indophenol Blue. Quantitative assessment of the effect on bleaching rates became difficult, as an induction period exists with these combinations. That is, there is little apparent change in optical density after a short exposure, but several minutes later, bleaching of the exposed areas takes place while the film is in the dark.

Another polymer, Arochlor (Monsanto), when used as an additive to RJ-100, increased the speed even further. However, the Arochlor acts as a sensitizer, and the films cannot be completely desensitized. Therefore, RJ-100 alone was used as the polymer of choice throughout most of the project year.

When coated on a flexible substrate, RJ-100 tends to crack after a period of time. In October, a flexible polymer, Eastman alcohol soluble butyrate, ASB, was found which seemed to give as good results as RJ-100, without the disadvantage of cracking. A thorough quantitative comparison of bleaching rates in the two polymers has not been made, however. ASB is the current polymer of choice.

A polysulfone polymer has been tested which has the property that a coherent film of polymer can be peeled off a glass substrate. A film made up on glass and exposed and locked in the usual way can then be stripped from the glass and mounted or otherwise handled by the user. The dimensional stability of the detached films was not sufficiently high to warrant further effort.

B. Parametric and Exploratory Experiments

In this section, experiments designed to evaluate the conditions of use of the photographic system and to explore alternate systems are described.

1. Heat locking. The process of locking or fixing the film by means of heat has been under continuous scrutiny. Observations have been qualitative, for the most part, consisting of determining which of various time and temperature combinations lead to satisfactory heat locking. Heat locking conditions have been found to vary widely, and depend on the dye, the photosensitive agent, the polymer and its thickness, and the substrate. To illustrate, a Rose Bengal film will generally need a longer heat locking period than a similar film using Indophenol Blue. A film based on iodoform will generally lock more rapidly than one based on carbon tetrabromide. A polystyrene film will lock more rapidly than one based on carbon tetrabromide. A polystyrene film will lock more rapidly than a similar composition in RJ-100. A film on Mylar will lock in one tenth to one fifth the time of the same composition on a glass substrate. A thick film will take longer to heat lock than a thin film. In addition, thermal reactions take place in some cases. For example, Rose Bengal-carbon tetrabromide films cannot be heated above about 110°C or they will thermally bleach. As can be inferred from the above, it is necessary to determine the optimum heat locking conditions for each formulation independently. Most of the work has been done with films on glass. For films on glass, heating time roughly doubles for every ten degrees drop in temperature. At 110°C heating time for films on glass ranges between 30 minutes and two hours. The TMI film on Mylar tapes is locked completely in six to eight minutes at 110°C.

Several experiments were performed using vacuum to aid locking. These experiments were based on the hypothesis that locking is due to evaporation of photosensitive agent and that evaporation would be more rapid in a vacuum. Results were not consistent, and the improvement shown thus far does not indicate that vacuum will shorten the locking time appreciably.

2. Packaging. It has been observed that photobleach films are more sensitive when freshly prepared than after storage. The effect ranges from a loss of about 50% on storage for some months for some films to complete loss of sensitivity in two days for the TMI film described earlier. The effect is ascribed to evaporation of the photosensitive agent. It has been shown that packaging the TMI film in aluminum foil will prevent the loss of activity. It has also been shown that a TMI film with iodoform omitted will become sensitive if it is stored in a closed container containing iodoform. The iodoform vapor diffuses into the film and imparts photosensitivity.

Although experimentation on packaging has not been extensive, we feel that we have demonstrated that a reasonable shelf life with high sensitivity can be maintained for the photobleach materials through appropriate packaging.

3. Contrast control. Brief experiments to determine the effect of heating during exposure have been performed. H & D curves (optical density plotted against log exposure) were plotted for several runs on two samples of a Rose Bengal iodoform film. For one sample, the film was held at room temperature during one run, and heated by a stream of warm air during the other. The slopes of the respective H & D curves were 1.6 and 2.0. The second film was run with two, one and no heat filters interposed between film and light source during exposure. The slopes for these runs were 1.8, 1.9, 2.0. These experiments demonstrate that the slope of the H & D curve can be increased by heating during exposure. No experiments were run with photographic subjects, however, so the question of whether this procedure will affect photographic contrast is still not resolved.

If contrast control is desired for the TMI films, an additional processing variable is available. The temperature and time of post-exposure heating probably have an effect on the contrast and latitude achieved by the films. These effects have not been investigated as yet, and should have a high priority in any future work on these materials.

C. Mechanism Studies

Experimental studies on the mechanism of the photobleach reactions received much less emphasis than in the preceding year. Three of the experiments related to mechanism will be briefly discussed.

1. Acid formation. The experiments on the mechanism of anthraquinone dye bleaching consisted of illuminating samples of dyes in films with CHI_3 as photosensitive agent for successive short periods of time and obtaining absorption spectra after each exposure. The same dyes in ethanol solution were treated with successive small portions of concentrated hydrochloric acid, and again absorption spectra were obtained. The initial, final and intermediate spectra were similar in both cases, indicating that reaction with acid is responsible for the bleaching process. Further, a completely bleached film was dissolved off the slide, and sodium hydroxide added. The solution then changed color, to the original color of the dye. This latter experiment was also successful using Indophenol Blue, which is not an anthraquinone. It now seems reasonably certain that the mechanism for anthraquinone dye bleaching involves neutralization by strong acid formed from the photodecomposition of the photosensitive agent. Although the evidence is less clear for other dyes, it is probable that the same mechanism applies for all the reactions studied.

2. Azide process. As indicated above, the mechanism of the photobleach reaction is believed to be the reaction of an acid with a dye. Some dyes also change color, or bleach, in the presence of base. A photochemical reaction, the photolysis of sodium azide, was found in the literature which results in the formation of base, in this case NH_3 and OH^-. A film was made up using a dye which bleaches in base, in addition to the photosensitive agent, sodium azide. The film bleached when exposed to the strong 2537A Hg line, but not when exposed only to longer wavelength radiation. This observation supports the mechanism assignment, and also leads to a new photobleach process. The one dye examined did not transfer energy to the azide, in the way that some dyes transfer energy to iodoform in the "acid" photobleaching process. The process was not investigated further because of the very low wavelength required, which is not transmitted through glass or through most photographic materials.

3. Complex formation. Experiments on two methine dyes gave strong evidence for the existence of a complex between dye and iodoform. In these cases, film made up with dye and iodoform were considerably lighter in color than expected from the dye alone. They darken on heating to drive off iodoform, and then bleached when heated in iodoform vapor. None of the other dyes examined for this behavior responded in the same way. The results, however, are significant in that they demonstrate the formation of a complex.

These effects were very pronounced for the two methine dyes. In the more common situation, the formation of a complex leads to a slight shift of wavelength, and to small change in extinction coefficient. The careful, quantitative work needed to verify the formation of complexes of other dyes was not undertaken.

Another interesting experimental result can be explained on the basis of complex formation. Rose Bengal requires considerably more heating for locking in a given film than does TMI, and Rose Bengal transfers energy to iodoform, while TMI does not. The formation of a complex between Rose Bengal and iodoform, and the lack of a complex between TMI and iodoform would explain both of these observations. A complex between Rose Bengal and iodoform would tend to slow down the evaporation of iodoform, and would allow the transfer of energy from the dye molecule to its partner. Generalizing, it is probable that all dyes that transfer energy do so because they have formed a complex with the photosensitive agent, while those dyes that do not transfer energy are not involved in a complex.

IV. RECOMMENDATIONS FOR FURTHER WORK

Several alternative approaches to the exploitation of Photobleach Photography are available. The approaches to be discussed here are: (1) optimization of TMI film, (2) extension of TMI film to black, and (3) extension of earlier work.

1. Optimization of TMI film. The TMI film is essentially ready for use. It meets the requirements for a photocopy film, except for the blue color in place of black and the present lack of contrast control. If the film will serve the purposes for which it was designed, as we believe it will, then it should be put to use. For this to be done, further work is needed in the following areas:

a. Optimization of film formulation. Further experimentation with the relative proportions of the ingredients of the film should be done, as well as on coating procedures, and film thickness.

b. Standardization of exposure and development conditions.

c. Gamma control. The possibility of the control of contrast should be thoroughly explored.

d. Standardization of packaging.

e. Design and construction of equipment to be used by the customer in the utilization of the TMI film.

It is expected that the work in the first four of these areas would be completed in about six months, at a cost of about one fourth of that for the Phase II program. The design and construction of equipment could be done simultaneously, at additional cost.

2. Extension of TMI film to black. The investigation of the TMI film to determine a dye or combination of dyes which will produce a black film would be considerably more difficult than the optimization of the blue film. A large number of dyes must be screened to determine compatibility with the TMI film. Dyes must be found with the proper color, solubility, and sensitivity characteristics. Further, they should be dyes which do not transfer energy, while most of our experience has been with dyes which do transfer energy.

For a reasonable probability of success with this problem, a one year program at about the past year's level of effort would be required.

3. Extension of earlier work. The success achieved with the TMI film and the properties demonstrated by it have caused us to re-evaluate the desirability of continuing work along previous lines. It now seems clear that non-complexing dyes have a clear superiority from the heat-locking point of view. We therefore recommend that no further work be done with complexing dyes (such as Rose Bengal) in the immediate future.

4. Recommendation. We feel that the program for optimization of the TMI film, described in paragraph 1 above, would give the greatest value per program dollar. If the TMI film is put into use, and found useful, but the blue color remains a handicap, then the second program, for extending the TMI film to a black, should be implemented.

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V. ACKNOWLEDGMENTS

Many helpful and stimulating discussions held with [redacted] contributed much to the progress of the project. The laboratory work was done by [redacted] whose skill and ingenuity also contributed greatly.

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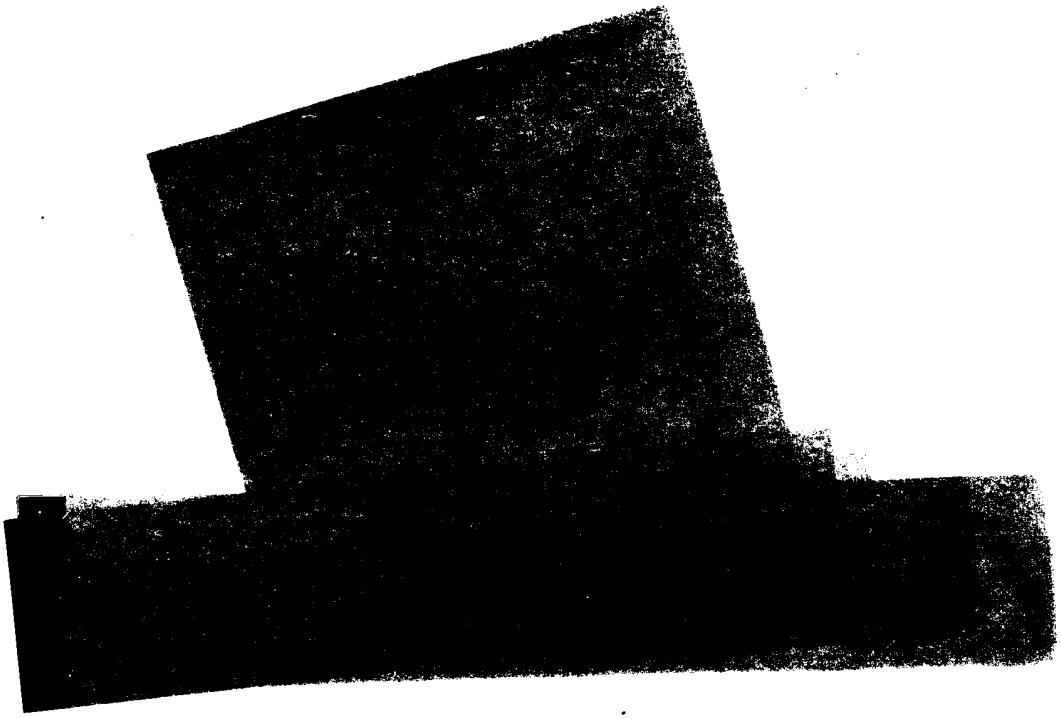


Figure 1a. Sample of TMI Film

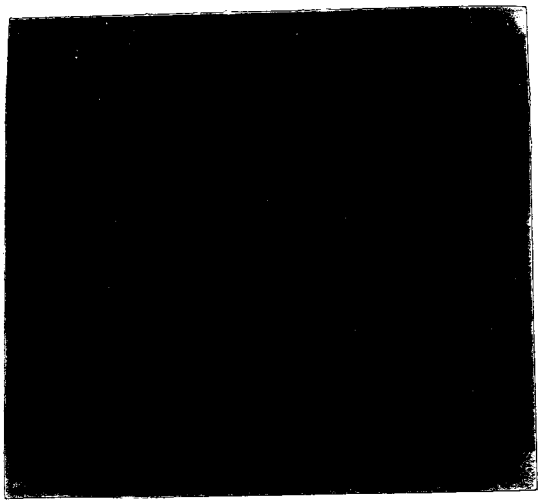


Figure 1b. Sample of TMI Paper

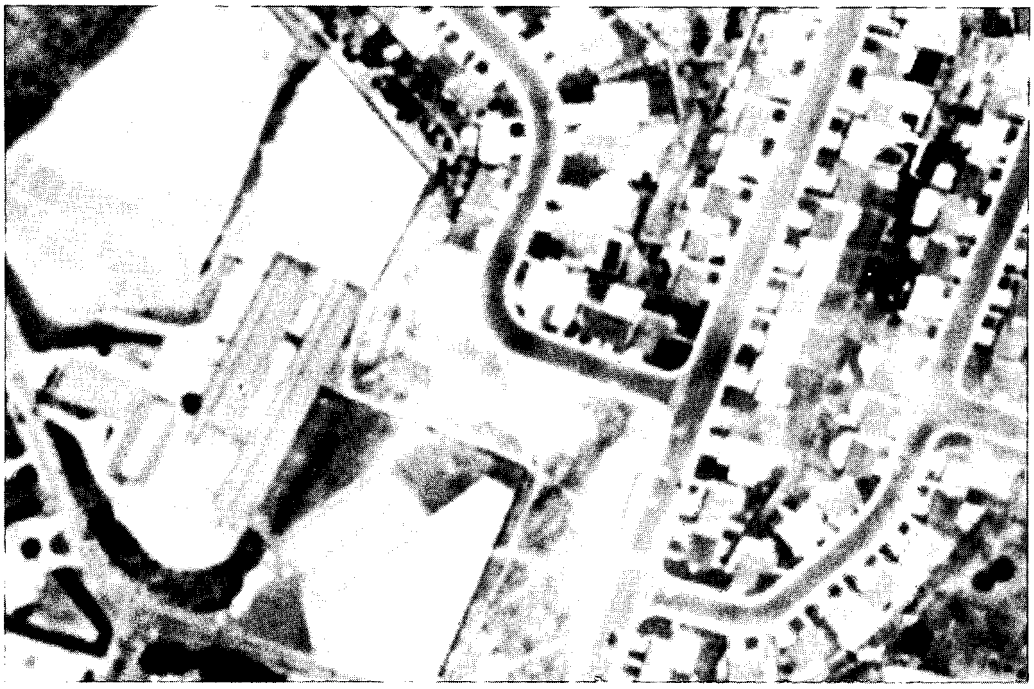


Figure 2a. Enlargement Made from TMI Film

Figure 2b. Enlargement Made from Silver Halide Original

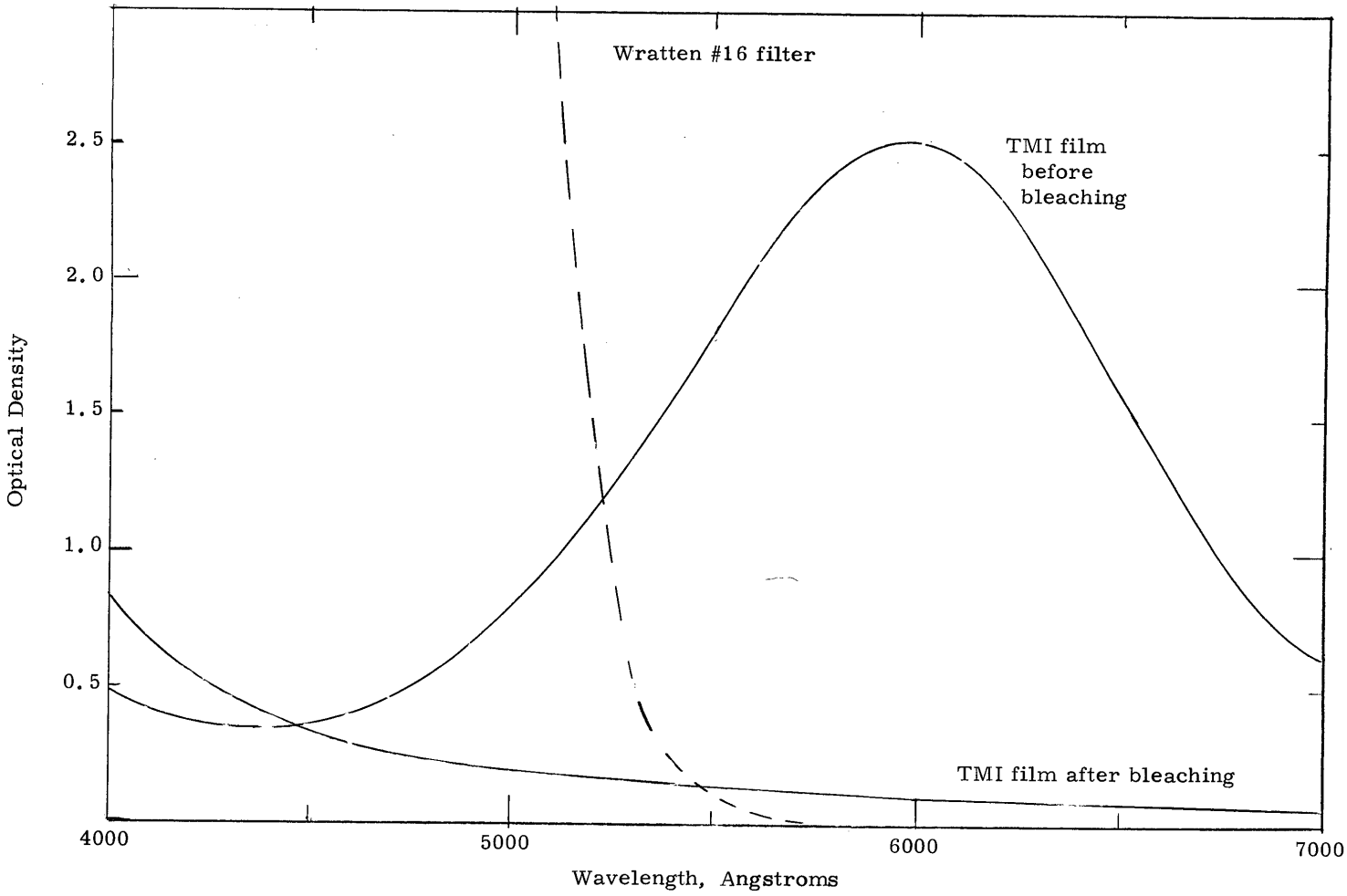


Figure 3. Absorption Spectrum of TMI Film

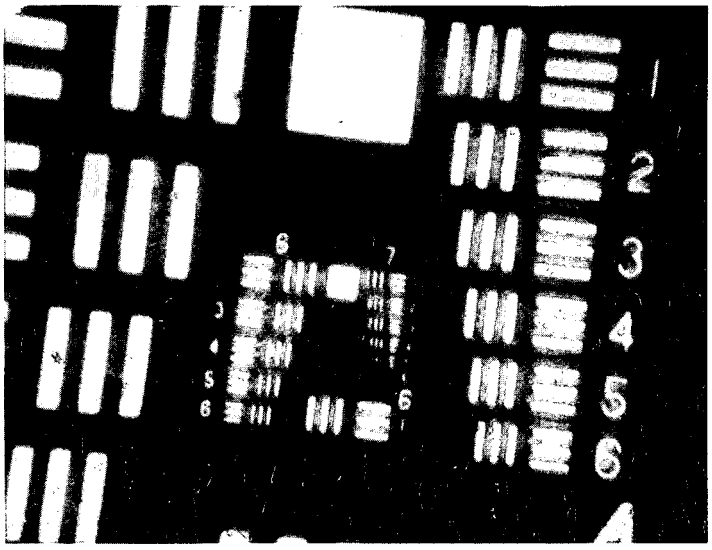


Figure 4. Photomicrograph of Resolution Chart on TMI Film

[redacted]

FINAL REPORT

Photobleach Photography

Phase II

30 November 1966

[redacted]

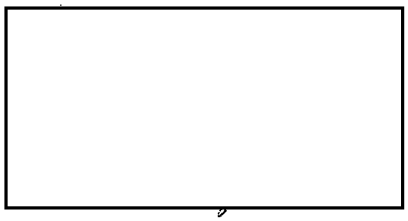
Next 22 Page(s) In Document Exempt

Approved For Release 2005/06/23 : CIA-RDP78B04770A002800030036-1

6 January 1967

Dear Will:

Attached are films which Max prepared in response to your telephone request. I hope these will be suitable for your requirement. If not, let us know.



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Attch.

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Contract No. [redacted]

Task No. 02

Progress Report No. 14 (FINAL)

Covering the period October 15 - November 30, 1966

Financial Status

25X1

Amount Authorized	[redacted]
Estimated Expenditures thru 11/30/66	
Funds Committed	
Funds Remaining	

*Subject to adjustment as final bills and credits are received.

Technical Status

The final technical report was submitted on 7 December 1966.

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[redacted]

6 January 1967

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INSTALL. INFO. FROM CONTR.	NA										
NPIC SITE PREPAR.	NA										
TEST SPEC. APPVL.	NA										
OPER. MANUAL APPVL	NA										
MAINT. MANUAL APPVL	NA										
ACCEPT TEST - EQUIP. DELIVERY	NA										
NPIC ACCEPT. TEST	NA										
FINAL REPORT FROM CONTR.											
FINAL EVAL REPORT											
COMPLETION											

REMARKS:

1. Time extension requested to 10 Nov
2.
3.
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