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[redacted]

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25X1 Attention: [redacted] Contracting Officer

Subject: PATENT REPORT - INTERIM

25X1 Reference: Contract [redacted]
Task Order No. 02

Gentlemen:

The patent docket listed below covers an invention made during work under Task Order No. 02 of Contract [redacted] 25X1

DOCKET	INVENTOR	TITLE
R&DC-75	[redacted]	Information Recording by Bleaching Dye Azide Composition

25X1

Since this invention was in the early stage of its development at the time it was docketed, it has not been decided whether a patent application should be filed. If the inventor's opinion of the work is supported by results of additional work, a patent application will be filed. You will be advised of our decision on this point as soon as the work reaches a point where a sound patent decision can be made.

A copy of the patent docket letter is attached.

Very truly yours

[redacted] 25X1

Contract Administrator

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Contract No. [redacted]

Task No. 02

Progress Report No. 12

Covering the period August 1 - September 16, 1966

Financial Status

25X1

Amount Authorized	[redacted]
Estimated Expenditures thru 9/11/66	
Funds Committed	
Funds Remaining	

Technical Status

Attached is a technical progress report covering the period of 1 August to 16 September 1966. Enclosures referred to in report are attached to original only.

25X1

[redacted]

23 Sept 1966

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Progress Report #12
Photobleach Photography Phase II

August 1 - September 16, 1966

Screening Experiments

The effort during August consisted of a continuation of previous work, i.e., screening of dyes and of mixtures. Several yellow dyes were tested, as were several mixture modifications without achieving any striking results.

DEMI and TMI

At the end of August, two new dyes were received and tested. These dyes, N, N-diethyl-2-methylindoaniline and N, N, 2-trimethylindoaniline, code names DEMI and TMI respectively, had been synthesized for this program. The work on these dyes will be the main topic of this report.

DEMI and TMI are blue dyes of similar structure, and related to Indophenol Blue, which has been extensively studied in this program. Films of DEMI or TMI sensitized by iodoform or carbon tetrabromide when exposed for 0.5 to 10 seconds (depending on light source, concentration of materials in film, and similar experimental factors) will show little or no evidence of bleaching. After heating for a few minutes, however, in an oven at about 100°C, the exposed areas will bleach resulting in a positive reproduction of the transparency used. The interesting aspect of this is that the contrast of the reproduction depends directly on the time of heating. That is, short heating times lead to images of low contrast, and as heating time is increased, the areas with greatest exposure decrease in density thus increasing contrast.

If use is to be made of this method of contrast control, the films cannot be heat fixed in the usual way, since heat fixing involves a longer heating period than that needed to develop the image. Several methods of solving this problem are possible. The simplest is to take advantage of the insensitivity of the films to light of wavelength greater than about 5000 A. Films protected by Wratten #15 filters, for example, can be exposed to intense light without damage. Such protected films have been exposed for ten minutes in a 500 watt projector without observable change. When viewed on a light table, the image in these protected films appears black or blackish green on a yellow background.

If heat locking is to be used, it is possible that contrast control can be achieved by careful control of exposure, once optimum heat locking conditions are determined. Heat locking for these materials is difficult, although it has been accomplished. In most cases in which it has been tried, the films have been over-exposed and have been almost completely bleached during heating. The

achievement of reproducible heat locking will require a program of extensive empirical testing of both exposure and heating conditions, utilizing reproducible films.

Conceivable fixing methods which avoid the problems of both the above alternatives include (1) a solvent wash by some solvent that will dissolve iodoform but not the dye or polymer, or (2) prolonged exposure to high vacuum without heating which presumably will remove the iodoform by evaporation. We have no direct experience with either of these methods.

Work with the above dyes has been done both on glass and on Mylar tape. Some time has been devoted in the last week to acquisition of some rudimentary tape coating technique. Some examples of tape, all of which were given the same exposure but different heating times, are enclosed with this report, together with the negative used in the exposure. Since the films are not heat locked, they should not be exposed to intense light without the protection of a yellow filter. A Wratten #15 filter is also enclosed.

Photometallic Process

A quite different technique for producing direct positives based on the "Photometallic Process" being studied in this laboratory has recently been proposed. In this process, a metal film (gold, silver, tin, and other metals have been used) is overlaid with a photoreactive material in a polymeric binder. On exposure to light, the metal surface is etched. The polymer film is then washed away. The remaining metal film is a direct positive reproduction of the mask used in the exposure. An example of a silver film on glass is enclosed with this report. Exposure was 45 seconds, to a 500 watt projector. It will be seen that the image looks metallic by reflected light, but looks blue black by transmitted light, as in a projector. The blue color is characteristic of light transmitted through thin films of silver. Other metals, particularly tin, do not have such windows in the visible region. The process is equally applicable on Mylar tape as on glass.

Plans for September-October

Work will be continued on the DEMI and TMI systems, and on films on tape. If desired by the sponsor, work on the Photometallic Process will be started.

The next report will be for the period September 19-October 21. The time remaining after October 21 will be devoted mainly to the final report.

25X1 Contract No. [redacted]

Task No. 02

Progress Report No. 11

Covering the period July 1966

Financial Status

Amount Authorized	[redacted]	25X1
Estimated Expenditures thru 7/31/66 . .		
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Funds Remaining		

Technical Status

Attached is a technical progress report covering the period of July 1966.

25X1 [redacted]

19 August 1966

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Progress Report #11
Photobleach Photography Phase II

July 1966

The effort during July was concentrated on the screening and evaluation of new dyes and mixtures, and on broadening understanding of previously used materials. Fourteen green dyes were obtained and tested. These showed low sensitivity but a few bleached to yellow. Four yellow dyes were tested with negative results. It was noted that a small amount of a green dye in a Rose Bengal film deepens the over-all color markedly, and results on a very fast film with good contrast between bleached (pale green) and unbleached (dark purple) areas.

Experiments have been run on several mixtures to determine heat locking conditions more precisely. It was found that high temperature (above 120°C) heat locking is not feasible for certain dye-PSA combinations, particularly Rose Bengal-CBr_4, due to thermal reactions, while several other combinations heat lock very nicely at high temperatures.

Plans for August. Screening of dyes is to be continued. Black mixtures are to be prepared for demonstration purposes. Some work will be done on systems which do not require heat locking. A 400 watt mercury lamp is to be put into operation, which will facilitate work with films needing near ultraviolet exposure.

25X1

Contract No. [redacted]

Task No. 02

Progress Report No. 10

Covering the period June 1966

Financial Status

25X1

Amount Authorized	[redacted]
Estimated Expenditures thru 7/3/66	
Funds Committed	
Funds Remaining	

Technical Status

Attached is a technical progress report covering the period of June 1966

25X1 [redacted]

19 July 1966

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Progress Report #10
Photobleach Photography Phase II

June 1966

The screening of blue and of green dyes has continued. In addition, some of the dyes were incorporated into black mixtures and evaluated. None of the dyes or mixtures showed outstanding properties. Several new dyes having appropriate color changes in acid have been ordered, and will be evaluated in July.

A brief experiment to determine the effect of heating during exposure on the H&D curve was performed. H&D curves (optical density plotted against log exposure) were plotted for two samples of a Rose Bengal-iodoform film. During one exposure the film was held at room temperature, while during the other the temperature was raised by a stream of warm air. The respective slopes of the H&D curves were 1.6 and 2.0. We have thus demonstrated that the slope of the H&D curve can be increased by heating during exposure. The question of whether such heating will affect photographic contrast during normal photographic exposure still remains to be answered, however.

We wish to request an extension in time for completion of the present contract, at no additional expense to the sponsor. The delay in the project has been caused by a manpower shortage which we have not been able to remedy. One of the two technicians employed on the project took a leave of absence during April and May in order to complete the requirements for his Bachelor's degree. Instead of returning to the project in June, as scheduled, he accepted a professional position elsewhere. We have not been able to find a satisfactory replacement for him as yet. At the present level of activity, we estimate that the project will be completed by November 10, although an earlier date is possible should appropriate personnel be found. The additional time requested will make it possible for us to complete more satisfactorily the requirements of the present program with the personnel now available.

Plans for July. The screening of dyes and evaluation of mixtures will be continued. Quantitative work on the effect of temperature on exposure parameters will be commenced.

25X1

Contract No. [redacted]

Task No. 02

Progress Report No. 9

Covering the period May 1966

Financial Status

Amount Authorized	[redacted]
Estimated Expenditures thru 5/29/66	
Funds Committed	
Funds Remaining	

25X1

Technical Status

Attached is a technical progress report covering the period of May 1966.

25X1 [redacted]

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Progress Report #9
Photobleach Photography Phase II

May 1966

Evaluation of mixtures continued as the major effort in May. Formulations based on Pinacyanol and Rose Bengal appeared very promising, showing good color and sensitivity properties. It was eventually determined, however, that Pinacyanol could not be completely fixed, as it has an inherent light sensitivity. As a result, Pinacyanol films which had been heat locked after exposure faded perceptibly when left in room light for a day or two. Work on Pinacyanol has therefore been terminated, and the search for a good blue dye reinstituted.

An apparatus has been built to investigate the variation of sensitivity of dye films with temperature. An approach to the control of contrast based on the temperature-sensitivity relationship has been formulated, and presented in the proposal for Phase III of this project. Although the major effort on this problem will be made during the next contract year, a brief attempt to demonstrate the feasibility of the approach will be made in late June or July, when the apparatus will be in operation.

Some photosensitive agents, which had not been previously tried, were tested briefly. Pentabromoethane proved to be slower than carbon tetrabromide, and hexachloroethane required ultraviolet exposure. Films were made up of various dyes in Saran (polyvinylidenechloride) and in polyvinylchloride (PVC), with the polymer serving as photosensitive agent. These films bleached with ultraviolet light, with the Saran films more sensitive than the PVC films. Some dyes proved stable to visible light in these films, while others bleached in white light. The behavior of the dyes in these media, with respect to wavelength sensitivity, was similar to that observed previously with added photosensitive agents such as iodoform.

Plans for June. Screening of dyes will be continued with emphasis on blue dyes having good color and sensitivity. Evaluation of mixtures will be continued. Further work on flexible substrates and on Saran films will be done, and the temperature studies will be initiated.

25X1

Contract No. [redacted]

Task No. 02

Progress Report No. 8

Covering the period April 1966

Financial Status

Amount Authorized	[redacted]	25X1
Estimated Expenditures thru 4/30/66		
Funds Committed		
Funds Remaining		

Technical Status

Attached is a technical progress report covering the period of April 1966.

25X1 [redacted]

1 June 1966

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Progress Report #8
Photobleach Photography Phase II

April 1966

The major effort during April was in the screening of dye-photosensitive agent combinations. A large number of such systems were prepared and run. Pinacyanol, a blue dye with good properties, was processed at the end of the month. Pinacyanol gives a deep blue, with high optical density available in the wavelength range of 540 to 650 nm. Bleaching properties are good, with an almost colorless product obtained in some examples. Sensitivity is moderately high.

A second field of activity was in the use of vacuum during heat locking. Several experiments were performed to see if vacuum would increase the speed of heat locking. Contradictory results were obtained. Further work on this is necessary.

During the heat locking experiments, it was found that exposure of the slides while warm would increase the photographic speed markedly. The potential value of this observation lies in that it gives us the ability to vary the sensitivity of a given material, and probably the gamma, although this is by no means certain as yet.

Plans for May

Mixtures of dyes based on Pinacyanol and Rose Bengal will be investigated. Vacuum heat locking measurements will be continued. Apparatus will be designed and constructed for constant temperature exposures so as to measure the variation of sensitivity with temperature quantitatively, and to determine whether or not temperature variation is a feasible means for gamma control.

25X1

Contract No. [redacted]

Task No. 02

Progress Report No. 7

Covering the period March 1966

Financial Status

25X1

Amount Authorized	[redacted]
Estimated Expenditures thru 4/3/66	
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Funds Remaining	

Technical Status

Attached is a technical progress report covering the period of March 1966.

25X1

[redacted]

20 April 1966

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Progress Report #7
Photobleach Photography Phase II

March 1966

Several additional blue and black dyes have been screened during March, and again there has been no discovery of a dye with outstanding properties. Similarly, screening of polymers and solvent systems is continuing. As an example of the polymer work, a polysulfone resin was investigated. The film formed from this polymer had the interesting property of being readily peeled off the glass support on which it was cast, resulting in a flexible, cohesive film with moderately good optical properties.

A series of runs was made on the effect of concentration of Rose Bengal and iodoform on quantum efficiency. The ratio of Rose Bengal and iodoform was kept constant, but the concentration of the reactants on the polymer film was varied. The light used was absorbed by the Rose Bengal only. The quantum efficiency proved to be relatively independent of initial concentration except at very low initial concentration, equivalent to optical density of 0.7 or less. For low concentrations, quantum efficiency was lower than at higher concentrations.

A small vacuum oven was obtained for further heat locking experiments. The experiments which had been reported previously were performed in a glass apparatus that was inconvenient to manipulate and to regulate. Preliminary results indicate that the new equipment may prove quite useful in these experiments.

Plans for April

Screening of dyes and polymers is to be continued. Tests on heat locking under vacuum will also be continued. Further effort in synthesis of a blue derivative of Rose Bengal will be made.

25X1

Contract No. [redacted]

Task No. 02

Progress Report No. 6

Covering the period February 1966

Financial Status

25X1

Amount Authorized	[redacted]
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Funds Remaining	

Technical Status

Attached is a technical progress report covering the period of February 1966.

25X1

[redacted]

8 April 1966

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Progress Report #6
Photobleach Photography Phase II

February 1966

Several blue and black dyes have been screened for photoreactivity using white light and also ultraviolet. Results so far have been disappointing in that none of the dyes examined has shown any improvement in properties over those already in use, such as Indophenol Blue. This screening is being continued. In addition, screening of polymer and solvent systems is continuing, both to provide further compatibility capability, and in the hope of finding polymers that will act as sensitizers. Among the dyes investigated were some interesting cyanine dyes with good color and reactivity properties, but which were not sufficiently soluble in any of the polymers we have yet used to make a dark film. Hence the need for greater compatibility.

A comparison has been made of the quantum efficiency of the photoreaction of Rose Bengal with iodoform and with CBr_4. The measured quantum efficiencies were essentially equal, when light absorbed by the dye alone is used. This result is significant in that the transfer of energy from the dye to the photosensitive agent does not seem to depend on the bond strength of the photosensitive agent.

An experiment was performed to see if loss of speed of the films on storage is due to loss of residual solvent. Several identical films were made up, and some were sealed into polyethylene bags. Rates of bleaching of the fresh film, of film stored in the bags for a month, and films stored in the customary box for a month were compared. The results indicate that storage of these particular films in polyethylene results in about 25% less loss in sensitivity. Other types of packaging and other types of films will be investigated in the future.

Plans for March

Screening of dyes and polymers is to be continued. In addition, a series of runs is planned to determine the effect of local concentration (at constant ratio of reactants) on sensitivity. Preparation of derivatives of Rose Bengal which are expected to be blue will also be commenced.

III. INTRODUCTION; OBJECTIVES AND PRESENT STATUS

Photobleach Photography is a process in which a dye or mixture of dyes, in combination with a photosensitive agent, bleach or change color upon exposure to light. The process is dry, non-reversible and results in continuous tone, high resolution images. Since the dyes are bleached by light, positive images of positive transparencies are obtained. Heating fixes the film so that it is no longer sensitive to light.

The objectives originally proposed for this process were those to have been achieved ultimately in a long range program of research and development. More recently, a more limited set of objectives have been specified. The modifications have been based on the properties immediately desirable in a practical, useful film, and on the experience derived during the course of the program.

The short term objectives to be attained are as follows:

1. Black and white (or colorless) film, with D_{max} = 2.0 or more, over the visible region, and D_{min} = 0.1 or less.

2. Resolution capability of 200 lines/mm.

3. Response latitude of at least eleven steps of a standard step wedge.

4. Sensitivity such that a 4 x 5 copy can be made in 30 seconds or less, using a total power of 1100 watts for exposure and all associated equipment.

5. Ability to control the photographic characteristic curve and thereby vary gamma from 1.0 to 2.0.

6. Ability to utilize a variety of substrates for the photosensitive film, e.g. glass, flexible transparent tape with stability comparable to Mylar, and paper.

7. Fixing time of one minute or less.

8. Storage stability for a period of a year before exposure and six months after exposure.

9. Short time stability to room lights before exposure and/or fixing to eliminate dark room procedures.

Each of these objectives, except for the color characteristics and the control of contrast, has been achieved separately but not simultaneously. For example, rapid (one minute) heat fixing has not yet been accomplished without serious deterioration of resolution. The major objective of the present proposal is to achieve all of the nine objectives above simultaneously in the same material. As it is expected that the desired color characteristics will be achieved during the current program, the objectives of the present proposal are:

1. to develop a technique for the control of contrast, and

2. to develop methods for combining all the desired properties into one photosensitive medium.

A brief review of the present status of the current program will serve as an introduction to the detailed technical proposal.

A. Optical Density and Color. The attainment of the desired optical density range depends on the choice of a group of dyes, each of which will provide the desired D_{max} over some portion of the visible spectrum, and will individually provide a D_{min} somewhat less than the desired value over the entire visible spectrum. In addition, an appropriate combination of dyes of the group should give the physiological sensation of black. Films of individual dyes have been made which meet the above requirements, but combinations which meet all the requirements are not yet available. The best combination film thus far had a D_{max} averaging 2.5 through the visible spectrum, and D_{min} of about 0.3-0.4 in the region from 5000 A° - 7000 A°. At wavelengths below 5000 A°, D_{min} was considerably higher, resulting in a tan appearance.

Progress is being made in this aspect of the work. New combinations of dye and photosensitive agent are continuously being tested. It is expected that, at the present rate of progress, the requisite D_{max} and D_{min} over the visible spectrum will be available by the end of this program.

B. Resolution and Fixing. Theoretically, the ultimate resolution capability of the material is limited by the wavelength of light (about 1000 line pairs/mm in the visible region). In practice, the resolution may be affected by diffusion, particularly during the heat fixing step, and by mechanical vibration during exposure. A resolution of 350 line pairs/mm was demonstrated in a crude experiment very early in the program. However, pronounced loss of resolution has been observed in some samples after prolonged high temperature fixing.

Heating fixes the films by volatilizing the photosensitive agent. Practical fixing conditions depend on a combination of factors. For a given film, fixing time decreases by a factor of about two for every ten degree rise in temperature. To achieve a fixing time of one minute, a temperature of about 160°C is needed. At this temperature, resolution is severely degraded in our materials, and Mylar is badly distorted.

Heat fixing has been done almost entirely in a conventional laboratory oven. Several experiments have been performed in a vacuum oven, and others with an infrared lamp. Other techniques such as forced hot air will also be tried. The evidence so far is not conclusive but seems to indicate that considerable modification of the presently used films and techniques will be needed for short time heat fixing to be effective. One such modification is based on the observation that heated films exhibit much greater sensitivity than films at room temperature. If a heated film is used to provide increased sensitivity, a smaller amount of photosensitive agent can be used, and thus reduce fixing time. This solution to the problem is undesirable, however, since the temperature control of the film will be necessary for other purposes to be discussed later.

C. Latitude. A response latitude of fourteen steps has been demonstrated on representative materials. There seems to be no reason to believe that the latitude response will be seriously affected by the nature of the materials used, as long as similar colors are employed. The more nearly the material meets the color specifications, the greater the latitude it will show, because of the eye response, and because of the density range available.

D. Sensitivity. The sensitivity requirements in the list of objectives is stated as an operational requirement because the terminology developed for silver halide materials is not readily applied to photobleaching materials. It is more appropriate to define the task to be accomplished, than to specify arbitrary numbers for sensitivity, which might prove either insufficiently high to accomplish the task, or unnecessarily high for that task.

For comparison of dyes, formulas have been developed which give a number for the sensitivity which is related to that of silver halide materials under specific conditions. The formulas have the form

$$S^a = \frac{0.147a}{t_a w (100 - T_{av})}$$

where S^a is the sensitivity value based on a change in optical density of a units from the initial optical density,

t_a is the time, in seconds, to achieve an optical density change of a,

w is the energy falling on the film in mw/cm^2,

and therefore $t_a w$ is the exposure in $mw\text{-}sec/cm^2$,

and T_{av} is average percent transmission of the film during the exposure.

The exposure needed to achieve a darkening of 0.1 optical density unit in a reference silver halide film, ASA = 1.0, gamma = 1.0 is used as a parameter in the above formula. S^a, the sensitivity, is the ratio of that exposure of the silver halide film to the exposure needed to effect a bleaching of 0.1 density unit of the photobleach film under investigation. In that sense, S^a is a direct comparison of photobleach material sensitivity with the standards set for silver halide materials. Several individual dyes which meet the operational sensitivity requirement have been derived. Some are an order of magnitude more sensitive than the minimum specified. The sensitivity values for these materials are about 2×10^{-6} to 3×10^{-5}.

E. Contrast Control. No experimental work has yet been done on this problem. An approach to the achievement of contrast control is discussed in Section IV, B, and constitutes a major portion of this proposal.

F. Substrates. Most of the photosensitive films have been cast on glass. Some of these films can be stripped from the glass backing and used as flexible films. Other films have been cast on Mylar or other flexible substrates, and on paper. Dye-photosensitive agent combinations have been absorbed by paper, and also by Mylar. Although the properties of the materials absorbed by paper are rather different from those of the polymer films cast on transparent substrates, there do not seem to be any fundamental limitations to the use of all of these substrates.

G. Material Storage. The present materials exhibit a sensitivity decrease in the first few days after preparation. The sensitivity subsequently remains relatively constant or decreases very slowly for long periods of time. The sensitivity loss is estimated to be a factor of about 2 to 2.5 over a year. Packaging of the materials reduces the loss of sensitivity, and may eventually eliminate it. Further, the sensitivity loss can be eliminated by warming the materials. Although not yet

investigated quantitatively, it is believed that the sensitivity loss is due to loss of residual solvent, or to slow air oxidation.

Exposed materials can be stored indefinitely in the dark without fixing. After fixing, some materials can be exposed for long periods to bright light sources. Others have proven inherently light sensitive and can only be exposed to moderate intensities, as on a light table, for periods of a few hours. Dyes in this last category will not be used in the final film.

H. Handling in Room Light. Very few of the formulations prepared to date are sufficiently sensitive so that handling for several minutes in normal room light produces noticable degradation of density. Exposure for long periods (hours), however, produces bleaching.

IV. TECHNICAL PROGRAM, PHASE III, 1966-1967

The primary goal of the Phase III program will be to develop a film meeting all of the objectives listed in the preceding section simultaneously. In order to do this, three problems remain to be solved. The first, derivation of a black and white film of appropriate D_{min} and D_{max}, is expected before, or very early in Phase III. The discussion in this technical proposal will therefore be limited to the other problems, i.e. very rapid fixing without loss of resolution and without damage to flexible film substrates, control of contrast, and the combination of all the desired properties in one photosensitive film.

A. Film Fixing. The materials developed to date are not suitable for rapid fixing. As shown previously, temperatures necessary for one minute fixing degrade resolution and produce distortion in these materials. The materials can be modified in several ways in order to obviate the problem. Materials which avoid the necessity for fixing present the most promising approach. In this method, photosensitive agent-dye combinations are used which are sensitive only to ultraviolet light, and not to wavelengths found in common sources of illumination.

Another approach is to modify the fixing technique by using vacuum, forced hot air, pulse heating, infrared heating, or similar means. A third approach is to build into the film a chemical system that reacts with the photosensitive agent and deactivates it upon exposure to infrared, heat or some other post-exposure treatment. Finally, the use of thermosetting resins, thermally stable films such as polyphenyleneoxide, and very thin films may reduce the undesirable effects of heat fixing to the required degree.

A simultaneous attack on each of these approaches to the solution of the fixing problem is proposed. Each will account for approximately 10-20% of the total effort. The approaches which have been mentioned above are:

1. films sensitive to ultraviolet light only;

2. modification of present heat fixing technique by use of auxiliary techniques: vacuum, forced draft, etc.;

3. modification of materials so as to reduce undesirable effects of heat fixing.

Each of these approaches will be discussed below.

1. Films insensitive to white light. The primary effort thus far has been on films which are sensitive to white light. In order to avoid fixing problems, films sensitive only to ultraviolet would be useful. Two approaches will be taken. In the first, photosensitive agents will be sought which are transparent to visible light and which have sufficiently high bond strength so that visible light will not affect them. The basis for the suggestion of this approach lies in the observation that some dye-iodoform mixtures will bleach upon exposure to light absorbed by the dye, and others bleach only with light absorbed by the iodoform. If the iodoform is replaced by a photosensitive agent which absorbs only below about 3000-3400 A^{o}, and if dyes of the latter type, that is, dyes which do not transfer energy, are used, the films should not be affected by light from tungsten or fluorescent lamps. The major effort to date has been on dyes which transfer energy as they can utilize a higher proportion of the incident light than can the others, and thus appear considerably more sensitive to the tungsten sources routinely used for exposure. To utilize these materials effectively, an efficient mercury source will be built and compared with a xenon flash unit for effectiveness.

The most likely photosensitive agents are compounds containing several chlorine atoms. Of these, intriguing possibilities are polyvinylidene chloride and polyvinyl chloride. These compounds are polymers and can act as the film material as well as the photosensitive agent. Halogenated polymers are known to undergo chain decompositions. When the elements of HCl are removed from polyvinyl chloride or polyvinylidene chloride a double bond is formed in the polymer. A chlorine atom is situated on the chain on a carbon atom adjacent to one of those in the double bond. Chlorine atoms in such structures are about one hundred times as susceptible to removal as those in other sites.[1] As a result, a chain reaction is possible, increasing the sensitivity of the system.

On the basis of this reasoning, films of Indophenol Blue in polyvinyl chloride (PVC) and in polyvinylidene chloride (PVDC) have been prepared and exposed to tungsten and to mercury sources. The PVC film showed no bleaching in a 500 watt projector for ten minutes, and the PVDC film only slight bleaching under the same conditions. Both films bleached under the mercury source, the PVDC film being considerably more sensitive.

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1. Boyer, R. F., J. Phys. & Colloid Chem., 51, 80 (1947)

The conditions for exposure and the sensitivity of dyes in these films will be determined. Similar work will be done with other commercially available materials such as chlorinated paraffins and rubbers which contain up to 70% chlorine and which may be more reactive for structural reasons. Polyvinylbromide[2] has been prepared and is expected to be more photosensitive than the chlorine polymers. However, it may prove sensitive to white light.

A second approach is to develop the azide process discovered in the spring of 1966. In this process, inorganic azides are illuminated with ultraviolet light and produce a base which then reacts with appropriate dyes, bleaching them. This is entirely analogous to the bleaching by acid which occurs with some dyes in the halide process. The main advantages of the azide process are that:

a. The bleached form of the one dye with which this process has been tried was more colorless (had a lower and more uniform D_{min}) than any film yet produced by the usual process.

b. A large number of dyes previously ignored because of insolubility can be examined, because the azides used are water soluble, and none of the other photosensitive agents are.

c. The azides are completely inert to light above about 3000 A^{o}.

The disadvantages are:

a. Considerable effort will be needed to find compatible and photographically useful polymer systems for these materials.

b. They may prove to be photographically slow.

c. A mercury light source would be needed, with its attendant inconvenience, or perhaps a powerful xenon flash unit.

2. Modification of heat fixing techniques. If the rate determining step for heat fixing is the diffusion of photosensitive agent through the polymer matrix to the surface, there is probably not much that can be done to improve the speed and effectiveness of heat fixing. If, however, heat fixing is a deactivation by reaction with oxygen or with

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2. Alina Ulinska, Zbigniew Mankowski (M. Kopernik Univ., Torun, Poland) Studia Soc. Sci. Torun. Sect. B2(2), 16 pp. (1960)-Chem. Abstr. 45, 5270d

polymer or if a reaction of some sort (a "fixing reaction") can be initiated by heat but not by ultraviolet and/or visible light, then heat fixing can be made rapid and effective simultaneously by environmental manipulation. A search for a fixing reaction is a large undertaking, and will not be attempted except as a peripheral activity. It does seem worthwhile, however, to attempt to improve the efficiency of heat locking by means of forced warm air and by investigating the effect of oxygen and of selected additives on heat locking.

3. Modification of materials. High temperature heat fixing affects dimensional stability and resolution. Polymers exist which show much greater dimensional stability to high temperatures than those which have been investigated. One such polymer is polyphenylene oxide, PPO, recently developed in this laboratory. These polymers will be investigated both as a medium for carrying the dye-PSA combination, and as a flexible substrate to be coated. Coatings must be made as thin as feasible, since fixing time at a given temperature is expected to vary exponentially with film thickness. Thus, high temperature polymers which are also good solvents for the dye-PSA systems are needed.

If such high temperature polymers prove effective as substrates but not as solvents, thermosetting polymers may be used as solvents. These materials cross-link on heating, and thus reduce diffusion. Since the dye molecules are much larger than PSA molecules, dye diffusion will be affected to a greater extent than that needed for fixing. This effect may be sufficient to maintain the needed resolution during high temperature fixing.

B. Contrast Control. Recent experiments have indicated that the sensitivity of photobleach films is markedly increased when they are illuminated while warm. In one experiment the sensitivity was increased by ten times for a temperature rise of about 40 degrees above ambient. These results point to a method for controlling contrast. The data are not yet sufficiently quantitative for an accurate estimate of the control available.

Theoretical considerations indicate, and some experiments performed seem to bear this out, that all photobleach materials will have similar H&D curves (Density D versus log Exposure E), differing only with respect to displacement along the log E axis. A single material, at different temperatures, should also have similarly displaced parallel H&D curves. As temperature is raised, the curve is displaced to lower log E values. If, however, temperature is changed during exposure, the shape of the curve will be changed, and hence the slope (or gamma) will be changed also. If the material is heated during exposure, thus

increasing sensitivity, the slope will increase and conversely, cooling during exposure will decrease the slope. The measured slopes of photobleach materials are 0.9 to 1.0, with sign opposite to that of silver halide materials. This means that heating during exposure will be the preferred mode, and fortunately, is experimentally easier than controlled cooling. In this regard, experiments have been carried out in this laboratory on the rapid heating of flexible films by infrared radiation. Temperatures of 40 to 50 degrees above ambient have been achieved in such films in less than one second with moderate infrared sources. These experiments indicate that the necessary rapid, uniform and controlled heating of the films will not present undue experimental difficulties.

The objective of contrast control is to render visible distinctions between images with small optical density differences. Another way of achieving this using photobleach materials is to overexpose, when the desired detail is in areas of high optical density, and underexpose in areas of low optical density. For example, a rough calculation indicates that areas of the original of optical density 1.70 and 1.71 can be rendered in the photobleach copy as 1.00 and 1.025 by an overexposure of 25 times. This renders a 0.6% difference of density into a 2.5% difference. Although any portions of the original with a density below 1.2 to 1.4 will be washed out, the contrast on the shadow area will be increased by a factor of four.

We propose to allot 30% of the effort of this program in Phase III to contrast control, the major portion of this time to the technique of varying gamma by varying the temperature, and a minor effort to ascertaining the parameters for over or underexposure. Heating techniques to be investigated will include two or more of: infrared, conductive heating, induction heating or radio frequency heating.

C. Final Film Formulation. The end product of Phase III should be a film which simultaneously meets or comes close to meeting all nine of the requirements listed at the beginning of this proposal. It is apparent that changes made to improve one characteristic may affect the accomplishments made on another property, either favorably or adversely. The detailed design of the final film will depend on the technique adopted for the solution of the fixing problem. For this reason, the major effort in the first half of the program year will be spent on the three approaches to fixing. When a decision has been made on the approach to be used, work will proceed on the choice of materials to optimize the properties of the over-all film. It is expected that the design of the film will be sufficiently definitive at the mid-point of Phase III for initiation of the design of the apparatus to be used with these materials.

The final film will be available, at the user's choice, on flexible substrates or on glass plates. A printing paper will also be available. However, since paper materials have a low priority in this program, they may not be as satisfactory as the transparent materials.

D. Summary of Technical Proposal. The work to be done is to be apportioned as follows:

1. Fixing - approximately 45%
   a. system insensitive to white light
   b. heat fixing techniques
   c. high temperature materials
2. Contrast Control - approximately 30%
   a. gamma control
   b. exposure control
3. Film Optimization - 25%
   a. continuing improvements in dye and photosensitive agent combinations
   b. improvements in substrate: polymer formulation, tape and glass coating techniques, papers
   c. maximizing of over-all film performance

This program is designed to achieve essentially all of the objectives listed on page 3 in a single, practical film. It is expected that this will be achieved by the end of the program proposed herein.

E. Reports. It is assumed that Phase III will constitute a one year study. Monthly letter reports and a final summary will be submitted.

25X1

Photo Bleach
Project File

10017

CATEGORY Reproduction

PFN 10117 25X

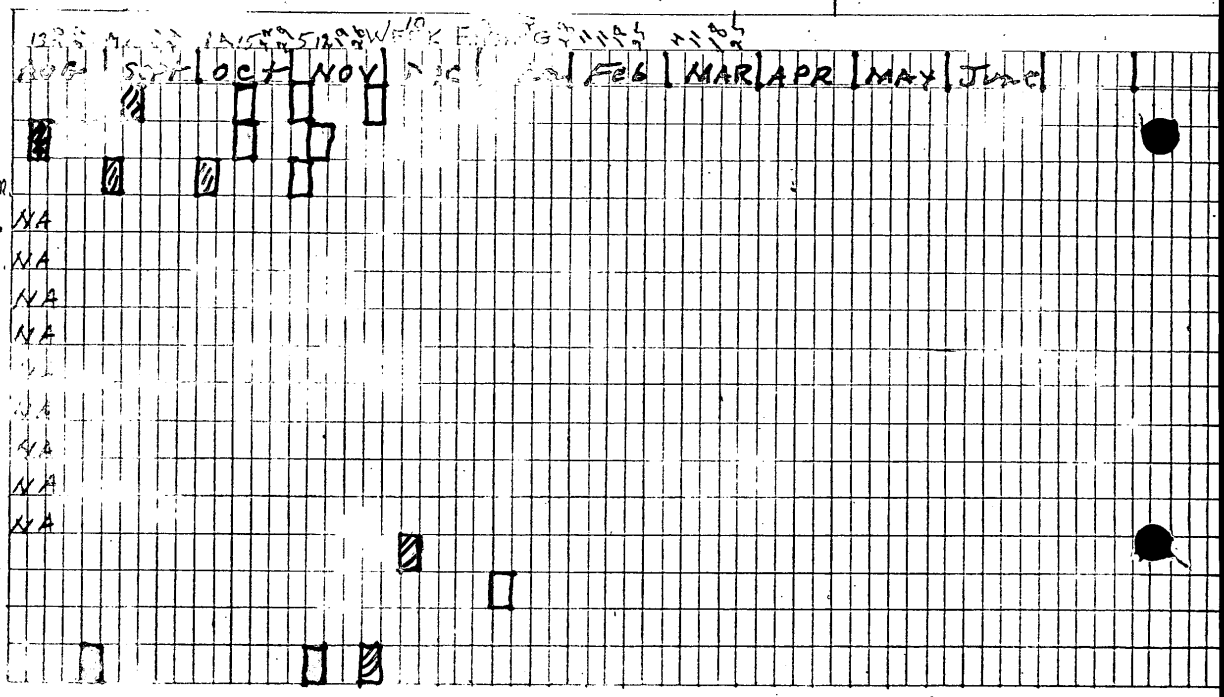
CONTRACT DATE 15 June 65

TITLE Photo Bleach Photographic

X1 CONTRACTOR

CONTRACT NO.

MONITOR COST



INSPECTION REPORTS TO O/L

TRIPS

MONTHLY REPORT FROM CONTR.

INTERIM REPORT FROM CONTR. NA

INSTALL. INFO, FROM CONTR. NA

NPIC SITE PREPAR. NA

TEST SPEC APPVL. NA

OPR MANUAL APPVL NA

MAINT. MANUAL APPVL NA

ACCEPT TEST- NA

EQUIP. DELIVERY NA

NPIC ACCEPT. TEST NA

FINAL REPORT FROM CONTR.

FINAL EVAL REPORT

COMMENTS

REMARKS:

1. Time extension for [illegible] NOV

2.

3.

4.

5.

8.

9.

10.

11.

CATEGORY Reproduction
PFN 10017
CONTRACT DATE 15 June 65

TITLE Photo Bleach Photography
CONTRACTOR
CONTRACT No.
MONITO
COST

25X1

WEEK ENDING

	AUG	SEPT	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUNE
INSPECTION REPORTS TO O/L											
TRIPS											
MONTHLY REPORT FROM CONTR.											
INTERIM REPORT FROM CONTR.	NA										
INSTALL. INFO. FROM CONTR.	NA										
NPIC SITE PREPAR.	NA										
TEST SPEC APPVL.	NA										
OPER. MANUAL APPVL	NA										
MAINT. MANUAL APPVL	NA										
ACCEPT TEST -	NA										
EQUIP. DELIVERY	NA										
NPIC ACCEPT. TEST	NA										
FINAL REPORT FROM CONTR.											
FINAL EVAL REPORT											
COMPLETION											

REMARKS:

1. Time extension requested to 10 Nov 7.
2.
3.
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10.
11.

PRECONTRACT WORK SCHEDULE

CATEGORY Reprd. Tech & Matls

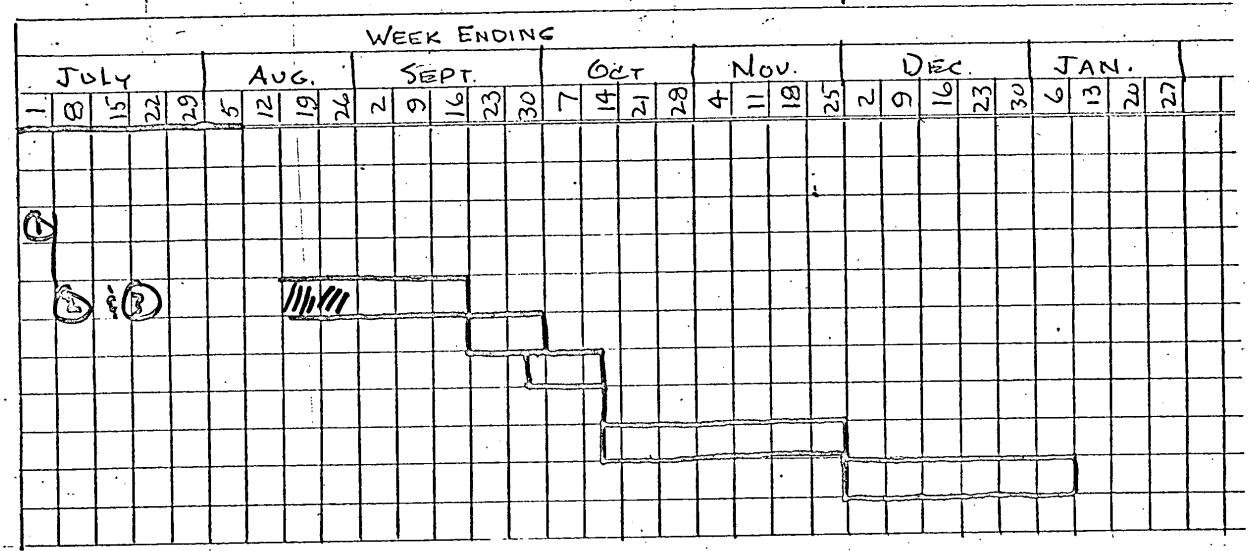
PFN 10017

DATE ASSIGNED

MONITOR

25X1

TITLE PHOTO BLEACH PHOTOGRAPHY



REMARKS:

1. Proposal Rec'd & Evaluated
2. STAFF STUDY Drafted - Held pending Compar. of Unconventional
3. Reproduction Techniques
4.
5.
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7.
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12.
13.
14.
15.

1-26-65

Interim goal

D max 2.00 D min 0.10 ? ✓

Resolution 2.00 L/mm ✓

~~ASA Speed Equivalent 0.001~~

gamma control 1. to 2. ✓

latitude 11 step of 21 step tablet OK ✓

storage capability before exposure 1 year
after exposure 6 months

color ~~Black & white~~ neutral

demonstrate capability of producing
4 x 5 inch contact print in not
more than 30 seconds

Power not more than 1100 watts ✓

finished product on flexible material ✓

Dr rose bengal

There is considerable question as to whether there can be any gamma control.

There may be a problem in inspection.

what is the fusing ten Tolerance

~~write tolerance [illegible] color~~

Approved For Release 2005/06/06 : CIA-RDP78B04770A002800040027-0

99073

PHOTOBLEACH PHOTOGRAPHY

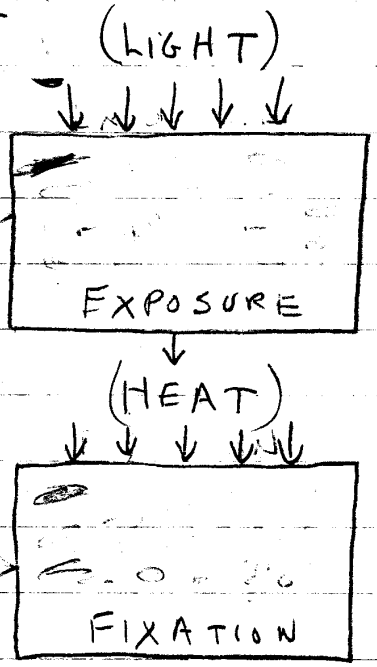
WHAT IS IT?

A dry-process, positive to positive, continuous tone, high resolution, rapid reproduction material.

Physical Description:

A film containing a deeply colored dye and a photosensitive reagent on a plastic base.

Mechanism:



Advantages

Dry Process

Very Rapid Reproduction (A few sec)

Positive to Positive Copies

Molecular Resolution (10^{-5} mm dia.)

Operator Experience unnecessary.

Potential Uses

Chips

Graphics

Current Status (Phase I) (FY 64)

Resolution ~ 350 ℓ/mm

Sensitivity ~ 0.001 – 0.01

Optical Density: D max 3.0 (over limited Spectral range)
D min 0.5 to 0.09 (incorporating results to date)

dye color : Various colors

Gamma Control : not yet investigated

Storage : not yet investigated

Objectives (Phase II) (FY 65)

Resolution > 400 ℓ/mm

Sensitivity: 0.01 to 0.1

Optical Density: Dmax 3.0 (over most of visible spectrum)
Dmin 0.1 to 0.05 (over " " ")

dye color: black to colorless

gamma Control: from 0.8 to 2.5

Storage: stable storage, before and after exposure,
> one years at ambient temps. & humidity.

Objectives (Phase III) (FY 66)

Formulation of one film which incorporates all of the required photographic characteristics achieved on several dye films in phases I & II