CONFIDENTIAL

164-64-20
Copy 2 of 3

25X1

[redacted]

Post Office Box 8043
Southwest Station
Washington, D. C. 20024

25X1

Attention: [redacted] Contracting Officer

Subject: [redacted]

Gentlemen:

Attached are two copies of a report entitled "Photobleach Photography, Phase II" dated 30 November 1966. This report is the final report under the subject task and completes the technical reporting requirements of the task.

Very truly yours,

25X1

[redacted]
Contract Administrator

Attch.

Declass Review by NGA.

GROUP 1
EXCLUDED FROM AUTOMATIC DOWNGRADING AND DECLASSIFICATION

CONFIDENTIAL

25X1

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

25X1

The final technical report was submitted on 7 December 1966.

[redacted]

6 January 1967

Distribution:
Technical Representative - three copies
File - one copy

25X1

Contract No. [redacted]

Task No. 02

Progress Report No. 13

Covering the period September 16 - October 14, 1966

Financial Status

25X1

Amount Authorized	[redacted]
Estimated Expenditures thru 10/9/66	
Funds Committed	
Funds Remaining	

Technical Status

Attached is a technical progress report covering the period of 16 September to 14 October 1966. Enclosures referred to in report are attached to original only.

25X1

[redacted]

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

Progress Report #13
Photobleach Photography Phase II

September 16, 1966 - October 14, 1966

Effort during the past month has been concentrated on TMI, one of the dyes initially reported last month, and on the mechanics of coating films on Mylar base. Considerable success has been achieved.

One problem that became apparent shortly after the previous report had been submitted is that the polymer used, RJ-100, becomes fragile several days after casting and cracks easily when the Mylar base is sharply bent. After screening several other polymers a new polymer was tried, and found to work satisfactorily. This polymer, an Eastman alcohol soluble butyrate, ASB, yields a smooth thin film of great flexibility.

The photographic properties of TMI in ASB are very good. Since experience with the polymer-dye-photosensitizer system has been less than two weeks, the proportions in the mixtures are far from maximized, and the best solvent system has not been determined. In spite of this, films of high quality can be made, as demonstrated by the samples enclosed with this report. One sample, a contact copy of a negative material, was exposed for five seconds to a 400 w mercury lamp, then heated for eight minutes in a 105°C oven. The other sample, a reproduction of a Kodak #2 Step Wedge, showing 13 steps, was exposed for 10 seconds, and heated for four minutes at 120°C. The speckled appearance shows the need for solvent and concentration optimization. Exposure times and heating times also need to be optimized. The samples, however, are heat locked and stable to light. One of our films has been exposed to a 1000 w projector for four hours with only minor bleaching.

Plans for October-November - Optimization of the TMI-ASB system will proceed. The writing of the final report of the year's work will be the major effort for the period.

25X1

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

Distribution:
✓Technical Representative - three copies
Contracting Officer - two copies
File - one copy

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.

X1

Contract No. [redacted]

Task No. 02

Progress Report No. 11

Covering the period July 1966

Financial Status

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

25X1

Technical Status

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

25X1

[redacted]

15 August 1966

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

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

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

25X1

Technical Status

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

25X1 [redacted]

19 July 1966

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

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]

17 June 1966

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

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.

5X1

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

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

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	
Funds Committed	
Funds Remaining	

Technical Status

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

25X1 [redacted]

20 April 1966

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

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]
Estimated Expenditures thru 2/27/66 . .	
Funds Committed	
Funds Remaining	

Technical Status

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

25X1 [redacted]

8 April 1966

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

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.

7073

25X1

Contract No. [redacted]

Task No. 02

Progress Report No. 5

Covering the period January 1966

Financial Status

25X1

Amount Authorized	[redacted]
Estimated Expenditures thru 1/30/66 . . .	
Funds Committed	
Funds Remaining	

Technical Status

Attached is a technical progress report covering the period ending 30 January 1966.

25X1

[redacted]

14 February 1966

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

Progress Report #5
Photobleach Photography Phase II

January 1966

The experiments described in the last report, on systems related to the dye Rose Bengal in RJ-100, have been continued. Sensitivity measurements of an improved formulation of Rose Bengal with iodoform in RJ-100 have shown greater sensitivity than any previous dye formulations, together with a relatively clean and uniform bleached color. The dependence of sensitivity on iodoform concentration was found to be linear. Sensitivity decreased with aging of the films. An experiment to determine whether packaging will prevent this loss of sensitivity is under way.

Rose Bengal, in the polymer in which it had been tested initially, had proved to be quite unsatisfactory. Therefore, other dyes which proved unsatisfactory in that polymer are now being screened for effectiveness in RJ-100. In particular, blue and black dyes are being examined, since these colors are most needed. As yet, a really satisfactory blue dye (needed for a good mixture) or black dye (to be used alone) has not been found, and a major portion of the effort for February will be expended in this direction.

Considerable experimentation using mixed solvents has taken place in order to increase the number of dyes that can be put into the polymer. So far, the solvents tried--benzene, ethanol, cellosolve, all in combination with THF--have decreased the sensitivity of Rose Bengal as compared with films made using THF alone. Other solvents will be tested in the future. In addition, a search for other polymers giving similar results is continuing.

Some experiments on the effectiveness of vacuum in shortening heat locking time were performed. The experiments indicated that the use of vacuum will decrease the time and the temperature of heat locking considerably. Optimum conditions have not yet been determined.

A meeting was held with the sponsor on January 28. It was mutually agreed that an interim goal, consisting of a film with specified requirements somewhat less stringent than those desired ultimately, would be set for achievement by the end of the current contract period. Tentative agreement on the following interim requirements was reached at the meeting:

1. 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 in not more than thirty seconds, using a light source of less than 1100 watts power.

3. Resolution 200 lines/mm.

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

5. Storage capability of one year before exposure, 6 months after exposure.

6. Gamma control of 1 to 2.

A final specification of the interim requirements is to be provided by the sponsor, after appropriate review.

It was pointed out at the meeting that achievement of goals 2, 3 and 4 have been demonstrated with materials developed to date. The major problem is to find a combination of dyes that will fit the first requirement, that of proper color and optical density, while retaining or improving the performance in the other respects. The storage requirements obviously cannot be completely demonstrated until a total of 18 months after choice of a final material, but continuing tests should give an indication of the storage behavior of the materials used. Finally, it is not known at present how gamma can be controlled in these materials.

The discussion of sensitivity at the meeting led to general agreement as to the inapplicability of ASA terminology to the photobleach materials. It is for this reason that sensitivity requirements are to be stated in the pragmatic terms of ability to perform a specific task under specified conditions rather than in terms of ASA speeds. For the time being, where numerical sensitivities are to be reported, they will be in terms of the photon sensitivity $S_p^{0.1}$ defined in

the final report (page 13) of the first year's program. $S_p^{0.1}$ is essentially the ratio of the exposure needed to cause an initial optical density change of 0.1 in a photobleach film to that needed to cause an initial optical density change (above fog) of 0.1 in a silver halide film of ASA = 1, gamma = 1 with normal processing.

The desirability of flexible film supports and also of a printing paper were made evident to us. We had planned to incorporate a small amount of work on these media into the program, but because of the sponsor's interest, work on flexible supports and on paper will be given more emphasis than in previous plans.

Plans for February

As noted above, the major effort is to be the continued screening of blue and black dyes, for sensitivity to visible and to ultraviolet light. Experiments with new polymers and with new combinations of solvents will continue. In addition, a derivative of Rose Bengal that may be blue will be synthesized in February or March. Experiments on vacuum effects in heat locking will be continued as time permits.

997073

25X1

Contract No. [redacted]

Task No. 02

Progress Report No. 4

Covering the period December 1965

Financial Status

25X1

Amount Authorized	[redacted]
Estimated Expenditures thru 12/26/65 . .	
Funds Committed	
Funds Remaining	

Technical Status

Attached is a technical progress report covering the period ending 31 December 1965.

25X1

[redacted]

18 January 1966

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

Progress Report #4
Photobleach Photography Phase II

December 1965

In the course of screening experiments, it was observed that a few dyes in a hitherto untested polymer bleached at rates several times faster than in other polymer matrices tried previously. This result is in contrast to our previous results, which had shown only slight differences in bleaching rate between the various polymers used. The effort in December was concentrated on the exploration of the properties of the new polymer, Monsanto RJ-100, as they affect the bleaching process.

Several interesting observations have been made. First, the effect is quite selective. Some few dyes experience very large increases, as much as a factor of four, in bleaching rate, while most do not seem to be affected. The dyes affected by RJ-100 are, so far, not the fastest dyes examined previously, but seem to have bleaching rates in RJ-100 approximately those of the fastest previous dyes. Second, induction periods are observed in most cases. That is, a short exposure leads instantaneously to a slight bleaching, but on storage in the dark for several minutes, the bleaching proceeds further. This effect makes quantitative evaluation of bleaching rate difficult and ambiguous.

For photographic purposes, the total bleaching caused by a given exposure is more important than the instantaneous bleaching. To determine the total bleaching as a function of exposure, the technique of moving the slide through the light beam described in Report #3, September 1964 - Black & White Films, is available. Readout can be accomplished at a series of times after the completion of exposure. However, as pointed out previously, the accuracy of this method is limited. Experiments, using this method, to study the factors affecting the induction period as well as to give values for effective bleaching rates have been started.

Plans for January

Further study of the effect of RJ-100 on bleaching, including study of the mechanism of the process, further delineation of type of dye affected, possible other polymers showing similar effects, and quantitative measurement of bleaching rates, will continue. If time permits, the study of the use of polyvinyl iodide as a multiplicative agent, discussed in the November report, and postponed because of the discovery of the polymer effect described above, will be started.

PG 707-3

25X1

Contract No. [redacted]

Task No. 02

Progress Report No. 3

Covering the period of November 1965

Financial Status

Amount Authorized	[redacted]	25X1
Estimated Expenditures thru 11/28/65 . . .		
Funds Committed		
Funds Remaining		

Technical Status

Attached is a technical progress report covering the period ending 30 November 1965.

25X1 [redacted]

7 Dec 1965

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

Progress Report #3
Photobleach Photography Phase II

November 1965

In trying to increase the quantum efficiency of the bleaching process, several additives were tested. One of these, N-vinyl pyrrolidone, increased the rate of bleaching of two dyes by about 20% and had little or no effect on two other dyes, each of the dyes having been chosen as representative of a class of dyes. Several related compounds were similarly tested, but none showed any positive results. Other related compounds have been ordered and will be tested as they become available.

A new photosensitive agent, tetraiodomethane, has been tested, but as yet seems to show no advantages over those previously used.

The mechanism studies indicate that the photobleaching is due to formation of acid, which then reacts with dye. 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. Further experiments, using materials such as lead azide which are much more photosensitive than sodium azide, and a variety of dyes, will determine whether this process has any inherent advantages over that now being studied.

Plans for December

In addition to continuation of the work described above, and previously, a start is to be made on a process for providing a multiplicative factor for the efficiency of the bleaching process. This will involve the synthesis of polyvinyl iodide, which is expected to undergo a photo-initiated chain reaction releasing the acid HI. This material will be incorporated in a film separate from the dye film, and will thus result in considerable advantages in the final film in terms of freedom from a fixing step, and in cleaner whites.

25X1

Contract No. [redacted]

Task No. 02

Progress Report No. 2

Covering the period through 31 October 1965

Financial Status

Amount Authorized	[redacted]
Estimated Expenditures thru 10/31/65 . . .	
Funds Committed	
Funds Remaining	

25X1

Technical Status

Attached is a technical progress report covering the period ending 31 October 1965.

25X1 [redacted]

9 November 1965

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

Progress Report #2
Photobleach Photography Phase II

October 1965

Quantitative measurements on the rate of bleaching of methine dyes have been continued. Measurements have been made using (a) white light, (b) monochromatic light at the absorption peak of the dye, and (c) light at the absorption peak of iodoform, at 362 mμ, for each of several dyes. An action spectrum was measured for one of these dyes.

Experiments on two methine dyes gave strong evidence for the existence of a complex between dye and iodoform. In these cases, films made up with dye and iodoform were considerably lighter in color than expected from the dye alone. They darkened 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, and may lead to a more detailed idea of the nature of the complex.

A new photosensitive agent hexachloro cyclopentadiene (HCP) has been used. HCP gives much less darkening in the visible region than does iodoform. One quantitative run, however, indicated that this material led to fairly rapid spontaneous reversal of the bleaching. Further work is planned to determine whether this is a general feature of HCP photobleaching.

Several experiments were performed to determine whether an electric field would increase the speed of photobleaching. The field was applied by corona charging the samples. There was no effect on the rate of bleaching of any of the samples tried.

Some experiments with the use of a flash system for exposure of films have been made. A relatively low energy flash system has been put together of about 900 joule maximum flash energy. This is being used to look at the performance of the films with flash exposure, and will be used later in studies of resolution capability of the films.

Plans for November

Continuation of the quantitative studies of the methine dyes, and of attempts to find a multiplicative process are planned. Studies of HCP, and similar materials, which are designed to improve color of the bleached films, and to increase quantum efficiency will also be continued.

Will give [redacted] Non-Revs.ble Film Study 97073.

Contract No. [redacted]

Task No. 02

Progress Report No. 1

Covering the period thru 30 September 1965

Financial Status

Amount Authorized	[redacted]
Estimated Expenditures thru 10/3/65 . .	
Funds Committed	
Funds Remaining	

Technical Status

Attached is a technical progress report covering the period ending 30 September 1965.

[redacted]

14 October 1965

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

Progress Report #1
Photobleach Photography Phase II

September 1965

The effort during September has been on the mechanism of anthraquinone dye bleaching, on quantitative measurements of methine dye bleaching, and on miscellaneous experiments on new materials.

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. The next step in the study of these materials, therefore, is to be a study of the feasibility of producing a chain reaction such that a single photon will produce many molecules of acid.

Some quantitative measurements have been made of the rate of bleaching of several methine dyes. Calculations have not been completed. Spectral studies have been started, similar to those described above for the anthraquinones. The dye studied was bleached by acid, but the results were not as clear cut as those in the anthraquinone case, due to overlap of the dye spectrum with that of photo-darkened iodoform. These studies will be continued with photosensitive agents absorbing further into the ultraviolet, so as to avoid this overlap problem.

Some new photosensitive agents were tried, and proved too reactive in the dark to be of interest. Diphenyl-picrylhydrazyl, a deeply colored free radical, was found to photobleach with iodoform, but was found to be too light sensitive without iodoform in the film to be of interest.

Plans for October

Continuation of the work described above is planned. This will include work on the multiplicative process for anthraquinones, and continuation of the quantitative studies of the methine dyes.

25X1

Contract No. [redacted]

Task No. 03

Progress Report No. 1

Covering the period thru 30 September 1965

Financial Status

25X1

Amount Authorized	[redacted]
Estimated Expenditures thru 10/3/65 . .	
Funds Committed	
Funds Remaining	

Technical Status

Attached is a technical progress report covering the period ending 30 September 1965.

25X1

[redacted]

14 October 1965

Distribution:
Technical Representative - three copies
Contracting Officer - two copies
File - one copy

Progress Report #1
Photobleach Photography Phase II

September 1965

The effort during September has been on the mechanism of anthraquinone dye bleaching, on quantitative measurements of methine dye bleaching, and on miscellaneous experiments on new materials.

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. The next step in the study of these materials, therefore, is to be a study of the feasibility of producing a chain reaction such that a single photon will produce many molecules of acid.

Some quantitative measurements have been made of the rate of bleaching of several methine dyes. Calculations have not been completed. Spectral studies have been started, similar to those described above for the anthraquinones. The dye studied was bleached by acid, but the results were not as clear cut as those in the anthraquinone case, due to overlap of the dye spectrum with that of photo-darkened iodoform. These studies will be continued with photosensitive agents absorbing further into the ultraviolet, so as to avoid this overlap problem.

Some new photosensitive agents were tried, and proved too reactive in the dark to be of interest. Diphenyl-picrylhydrazyl, a deeply colored free radical, was found to photobleach with iodoform, but was found to be too light sensitive without iodoform in the film to be of interest.

Plans for October

Continuation of the work described above is planned. This will include work on the multiplicative process for anthraquinones, and continuation of the quantitative studies of the methine dyes.

Non-Reversible Color - Study

Progress Report No. 13

Financial Status

25X1

Amount Authorized

Estimated expenditures
thru 30 August 1965

Funds Committed

Funds Remaining

Technical Status

The final technical report was submitted on 13 September 1965.

25X1

12/1/65

Distribution:
Technical Representative - three copies
File - one copy