AFCRL-68-0504

# SPECIALIZED PHOTOSENSITIVE MATERIALS FOR LASER RESEARCH

Charles W. Wyckoff, John D. Plumadore, and Ronald (NMI) Francis

EG&G, INC.
Crosby Drive
Bedford, Massachusetts 01730

Contract No. F 19628-67-C-0389
Project No. 8663

## FINAL REPORT

Period Covered: 1 July 1967 through 31 June 1968

Date of Report: 30 September 1968

Contract Monitor: George A. Vanasse
Optical Physics Laboratory

THIS RESEARCH WAS SUPPORTED BY THE ADVANCED RESEARCH PROJECTS AGENCY.

Prepared for

AIR FORCE-CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
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# ABSTRACT

The limitations of commercially available photographic materials for application in laser emission studies are described in terms of their spectral response, sensitivity level, short dynamic exposure range, and low tolerance to high energy densities. Commercially available XR film, which has a uniform response for visible light photography spanning nearly eight orders of magnitude, is not optimally suited for laser emission studies above 6900Å nor does its high optical density allow the film to endure energies greater than 0.1 joule/cm$^2$. The results of studies with silver halide and photochromic emulsions and with special film models specifically designed for use in recording laser emissions are summarized. The silver halide films not only have a $10^9$ dynamic range of exposure, but also are responsive to a broader spectral range including wavelengths in the one micron region. Furthermore, these films have exhibited toleration to energy densities of 45 joules/cm$^2$. Response to 10.6μ was found in photochromic films.

# FOREWORD

EG&G INC.

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This report was prepared by EG&G, Inc. on Contract No. F19628-67-C-0389 entitled "Specialized Photosensitive Materials for Laser Research." The work was performed in conjunction with Air Force Cambridge Research Laboratories, Office of Aerospace Research, United States Air Force and was sponsored by the Advanced Research Projects Agency. Dr. George A. Vanasse was the contract monitor.

The studies presented began in July 1967 and were concluded in June 1968. Dr. Ronald Francis undertook overall program responsibility under the direction of Mr. Charles W. Wyckoff.

Program areas and contributors were as follows: Mr. P. M. Paulsen, who was responsible for commercial XR film evaluations; J. D. Plumadore, C. H. Shaw and E. J. Ryan who were responsible for experimental silver halide emulsion formulation, coating, and evaluation; P. T. Sullivan and E. J. Curelop, who were responsible for photochromic and dye synthesis and non-silver halide systems evaluation.

This is the final report on Contract No. F19628-67-C-0389 and is issued by EG&G under Report No. B-3877.

Page

## ILLUSTRATIONS

FIGURE

ILLUSTRATIONS (Continued)

# SECTION 1
# INTRODUCTION

Many investigators using photographic films for the study of laser beams have encountered difficulties that have sometimes limited the usefulness of the results.[1-4] The difficulties center around the extremely high-energy density in laser beams and the inappropriate spectral sensitivity of the film. The insertion of an optical filter to attenuate the beam intensity to a more useful photographic level often introduces optical distortion and results in misleading information. If sufficient absorption occurs, the filter itself may be destroyed before a satisfactory image can be recorded. Optical filters that partially reflect and transmit the beam would appear to be a satisfactory solution to this problem. The reflected beam can be made to contain a small fraction of the energy of the main beam, thus effectively attenuating the energy to a photographically useful level. However, such filters have a finite thickness and are bounded by two surfaces, and both surfaces reflect a portion of the beam energy. The reflected portion, which is used for the photographic recording, is composed of two components that are displaced, and hence distorted, by an amount that is a function of the filter thickness. A photographic image so recorded may produce a distorted pattern of the laser beam. The exceedingly high energy density level contained in many laser beams often demands the use of more than one partially reflecting filter placed in the beam. The probability and extent of beam distortion increases with the number of filters used. However, if severe overexposure or even destruction of the film is to be prevented, some filtration with its accompanying degradation is required.

None of the films or plates currently employed for photographic recording of laser beam patterns has been specifically designed for this application. The films generally used are usually selected as the best compromise of available materials and leave much to be desired as an optimum choice. Neither the relative spectral respon‑e, nor the sensitivity level, nor the exposure latitude of commercially available films or plates is entirely satisfactory for investigating laser beam parameters.

Most photographic materials have been designed to obtain a permanent record of the pictorial scene as seen by a human observer. The spectral response of these films does not include the entire visible spectrum. In particular, the longer wavelengths of the visual red spectral region are not included in the response of most panchromatically sensitized photographic films. A visual impression of the recorded scene does not appear to be seriously degraded by a lack of recorded information beyond 6500Å where most pictorial films cease recording. From a scientific consideration, especially in the study of laser beams, the exclusion of photographic response to wavelengths longer than 6500Å is undesirable. Special photographic materials sensitized to respond to longer wavelengths is obviously a requirement for use with most laser beams where the energy is often emitted at considerably longer wavelengths.

In addition to the limitations in spectral response of photographic films, pictorial applications seldom require a total exposure scale exceeding three orders of magnitude, and most films respond within these limits. The density resulting from exposing a normal film to a level a thousand times in excess of threshold exposure is usually so high that useful detail information is lost through the diffusion and scattering of light within the image.

This relatively narrow exposure latitude is often a limiting factor in photographic investigations of laser mode stability as a function of pumping energy. The range in the energy density output of a laser under the conditions of different stimulation energies often exceeds greatly the recording capability of the photographic material. When the energy density output is known with certainty, filtration can be used to ensure optimal exposure within the desirable range of the film. However, the exposure is optimized only at the expense of the image degradation caused by the added filters. Frequently the laser output is not sufficiently predictable to permit exact optimization of the exposure and thus precludes a completely satisfactory photographic recording of the image. An example would be the inability to record any patterns which may exist around a mode at the same time that detail of the mode structure itself is being recorded.

Beam propagation in nonlinear media can best be investigated by recording the resulting changes in energy density with the ultrahigh-speed streak camera. The time resolution necessary to study the effects upon propagation of the nonlinear medium does not permit changing filters for exposure control. Thus, the image must be recorded within the limitations of the film. Both the mode stability and the beam propagation tests suggest that a special photographic material having a capability for responding over an extremely wide range of energy density is needed.

Methods have been devised through special processing techniques to increase the dynamic exposure latitude of certain films and to minimize the effects of light scattering and diffusion at high densities. One such method, demonstrated by Kodak, employs the Kodak-developed Bimat process and results in a significant increase in the useful exposure latitude of films such as Plus-X and Double-X Negative. Images that were exposed over a range approaching six orders of magnitude can be detected when using Bimat processing. Techniques have been developed that employ surface latent image processing while others use internal latent image processing in an effort to reduce the effects of high density scattering, thereby increasing the film's exposure latitude. These techniques tend to increase image detectability at high densities. Unfortunately, all these techniques reduce the slope (contrast) of the film's characteristic curve.

Although there is an improvement in detectability of heavily exposed images over that resulting from normally processed films, the resulting low-contrast images compromise the precision of detection and measuring because of lowered slope and nonlinearity of the total D-log E characteristic curve.

An interesting approach that overcomes the difficulties at low contrast with a nonlinear curve was reported by workers at Westinghouse Electric.[5] They used a partially reflecting mirror to divert a portion of the laser beam, and minimized the displacement of secondary reflections by using a very thin membrane as the mirror. In addition, they used a film which was designed with an exceedingly wide exposure latitude. This film, known commercially as XR film, was developed by EG&G, Inc. and is manufactured by Eastman Kodak exclusively for EG&G, Inc.[6] It has an apparent straight line response over an exposure range of one hundred million. With an effective slope of unity which uniformly spans eight decades of exposure, image detail and measurement precision are optimized. Like other photographic films, XR film was designed specifically to record in the visible spectral range from 3500Å to 6500Å. In addition, the most sensitive component of XR has been sensitized to respond at 6900Å, but with a narrow exposure latitude. The spectral sensitivity of the remaining elements, necessary to increase the dynamic exposure range, does not extend effectively beyond 6500 Å. Detailed photographic characterization of this film is given in Appendix A and in a recent article by Lehmbeck.(7)

Although it appears to have been successfully used for recording and quantitatively measuring the energy distribution in a ruby laser beam, even this film in its present state is far from an optimum choice for such work. The energy density levels contained in many laser beams are sufficiently great to cause destruction of most films, if used directly in the beam. The least sensitive element of XR film has a minimum useful sensitivity which enables it to record within approximately two orders of magnitude of the energy required to destroy the film. Greater separation is obviously needed between the destruction energy level and the minimum sensitivity level.

The spectral sensitivity of the current XR film is somewhat different for each of the elements of the film, and no attempt was made to match properly the levels for each element in the far red or near infrared region. As a result, the composite D-log E characteristic of XR film does not produce an effectively uniform curve at wavelengths greater than 6500Å, and noticable gaps in the total response are evident in the transition from one element to the other when using this material for far red laser-beam applications. Because most lasers emit at longer wavelengths, data reduction from XR images is less precise than it would be if the spectral sensitivity of each element was properly chosen for such recording. Like other normal photographic films, the sensitivity of XR in the far red and near infrared decreases rapidly, and the spectral sensitivity curves suggest that there is no response beyond about 7000Å. In spite of the apparent lack of far red sensitivity, XR film like many others does respond to the near infrared wavelengths of some ruby lasers, thus indicating lack of sufficient data in the spectral sensitivity curves for this film as well as other films.

Photographic emulsions that have not been spectrally sensitized are commonly referred to as color blind, and are primarily sensitive only to ultraviolet and the longer blue wavelengths of the visible spectrum. In most photographic applications films are not required to record exposure differences greater than a few hundred. For this reason, published curves showing the spectral sensitivity of such emulsions usually present only that range in sensitivity that is useful for general pictorial photography. Examination of a more complete spectral sensitivity curve reveals that even a primitive emulsion that has not been spectrally sensitized does indeed respond to red and even near infrared wavelengths although poorly.

Figure 1 presents a more complete spectral sensitivity curve for a non-sensitized emulsion and shows the relatively lower response of the emulsion at much longer wavelengths.

Large crystals of silver halide in photographic emulsions respond to lesser amounts of energy than do small crystals, primarily because of a greater surface area. Hence, the general level of spectral sensitivity may be raised or lowered in a more or less spectrally uniform manner by making the photographic emulsion with large or small crystals, respectively. However, during manufacture of the film the peak spectral response can be broadened towards longer wavelengths by adsorption of certain sensitizing dyes to the silver halide crystals. A silver halide crystal becomes sensitive to a different spectral region by the adsorption to its surface of a critical amount of a monomolecular layer of a dye sensitizer. When photons of sufficient energy are absorbed by the dye, a photoelectron is transferred to the crystal lattice where it becomes trapped and ultimately causes formation of a developable latent image. By proper choice of dyes, the silver halide crystals are made to respond more efficiently to wavelengths longer than those at the peak response of the primitive crystal. However, the native sensitivity beyond the broadened peak remains unaltered at its relatively low level. For photographic films including XR, even this low level of sensitivity is often too high for direct photography of a laser beam, and some means of attenuation must be provided.

Figure 2 illustrates the approximate photographic response of several available photographic films in terms of energy density in the 3500Å to 6500Å spectral region. The fastest film available today (Royal-X Pan or RXP) requires an energy density in the 3500Å to 6500Å region on the order of $10^{-9}$ joules/cm$^2$ incident upon the emulsion in order to produce usefully recorded information. Its range of linear recording,

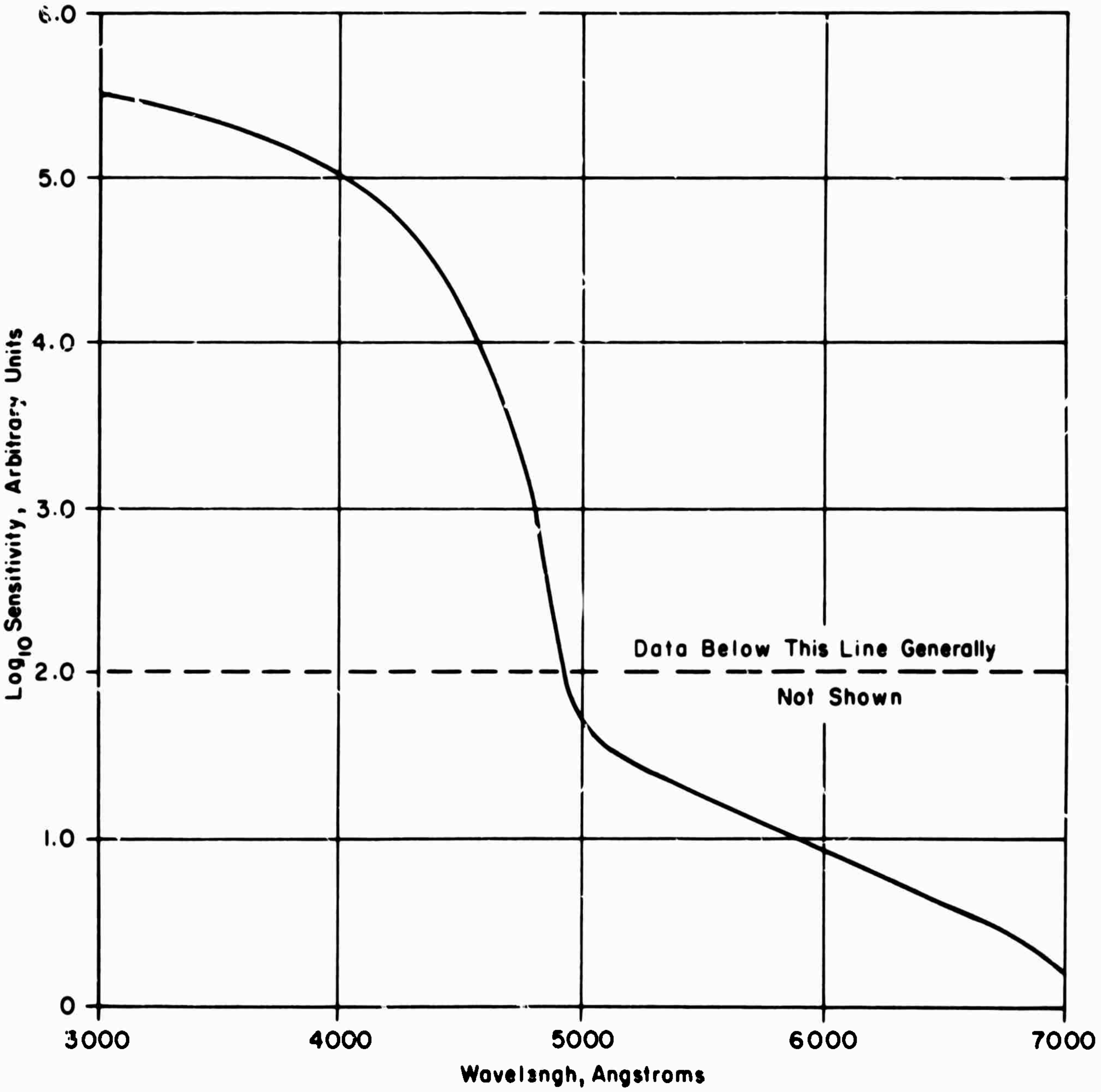

Figure 1. Relative spectral sensitivity of a primitive silver halide emulsion.

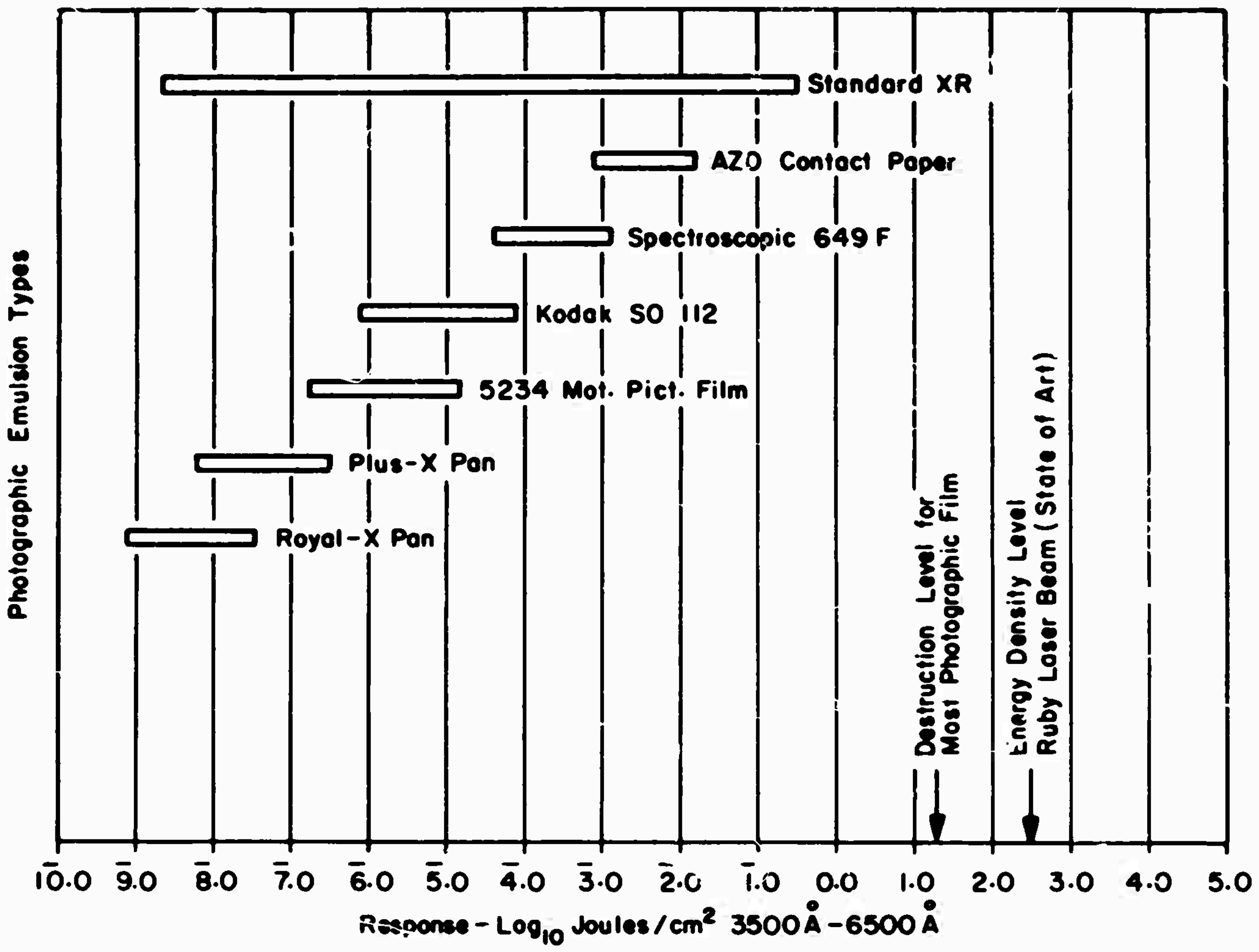

Figure 2. Diagram of energy density response for several available photographic emulsions exposed to a wavelength band of 3500 to 6500Å.

like that of most other photographic materials, is limited to a factor of less than one hundred. Thus, the maximum energy density that this film can accept and still produce useful measurement data is $5 \times 10^{-8}$ joules/cm$^2$. It may be noted that the first six materials shown in the figure, when used in combination, will record only slightly more than seven decades of energy density levels in the visible spectral region. The seventh, or XR film, shows a response range somewhat greater than all of the other emulsions combined.

The spectral output of a ruby laser is contained in a narrow band whose wavelength is beyond the sensitized peak for most commercially available photographic films. Figure 3 shows the exposure response for the same films displayed in Figure 2 except that all the exposing radiation is confined to a narrow band at 6900Å. This spectral band, which corresponds approximately to the output of a ruby laser, is beyond the peak for which the photographic films have been especially sensitized. It is of interest to note that the more-or-less uniformly increasing level in energy density required for the films displayed in Figure 2 is not present for the same films when exposed at the ruby laser output wavelength. All of the materials appear to be similar to one another in sensitivity with the exception of AZO contact printing paper and XR film. Because XR is composed essentially of three separate emulsions, there are noticable gaps in the exposure response that correspond to the transition between layers when the wavelength of the exposing radiation is confined to a band at 6900Å. This is caused by a mismatch in the spectral sensitization of each layer.

Alteration of the spectral sensitivity of this film during manufacture to optimize its response at 6900Å would eliminate the recording gaps between the layers. The effect of such sensitizing is illustrated

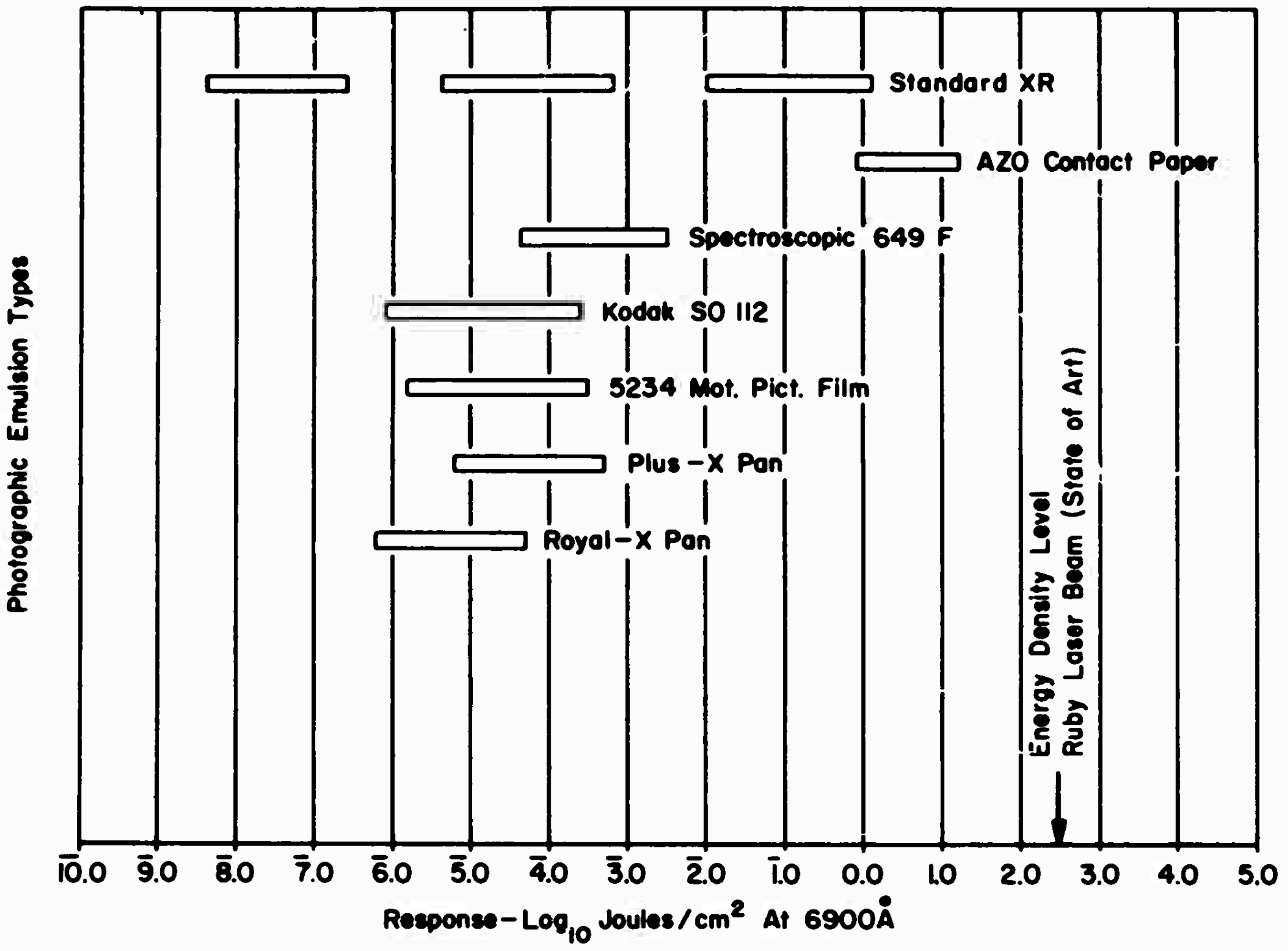

Figure 3. Diagram of energy density response for several available photographic emulsions exposed to a ruby laser wavelength of 6900Å.

in Figure 4 by the emulsion marked Modified XR (RXR). When so sensitized, this film will respond to 6900 Å nearly as efficiently as it does over the visible spectral range. Thus, the special modified XR film (RXR or Extended Red XR) could be used over a broad spectral range without degrading its wide dynamic recording image.

The first objective of the program was to extend the spectral sensitivity of XR film to peak at 6900Å.

At the present time, XR film is manufactured by Eastman Kodak exclusively for EG&G, Inc. An extension of the spectral sensitivity to peak at 6900Å has been incorporated in the fast element of this material and has not shown any adverse effects upon the characteristics of the film for normal applications.

The bottom element of XR film does not exhibit a uniform spectral response and shows a higher red response than it should. This effect is negligible for most pictorial applications, but is undesirable when the exposures are confined to the red spectral region. Therefore, it was advisable to make the spectral response more uniform in this element, especially with the extension of sensitivity to peak at 6900Å.

The second objective was a new film designated Laser XR (LXR). The film response of LXR would be as shown in Figure 4. As noted, the dynamic range of LXR would be significantly greater than the dynamic range of the spectrally modified XR. The construction of LXR would result in a film capable of withstanding greater energy density before destruction. Thus, with a wider dynamic range and a greater destructive level, less filtration would be required in the laser beam and recording distortion would be reduced. The spectral sensitization of LXR would be broadened in the near infrared, thus making this film suitable for mode stability studies of different types of lasers.

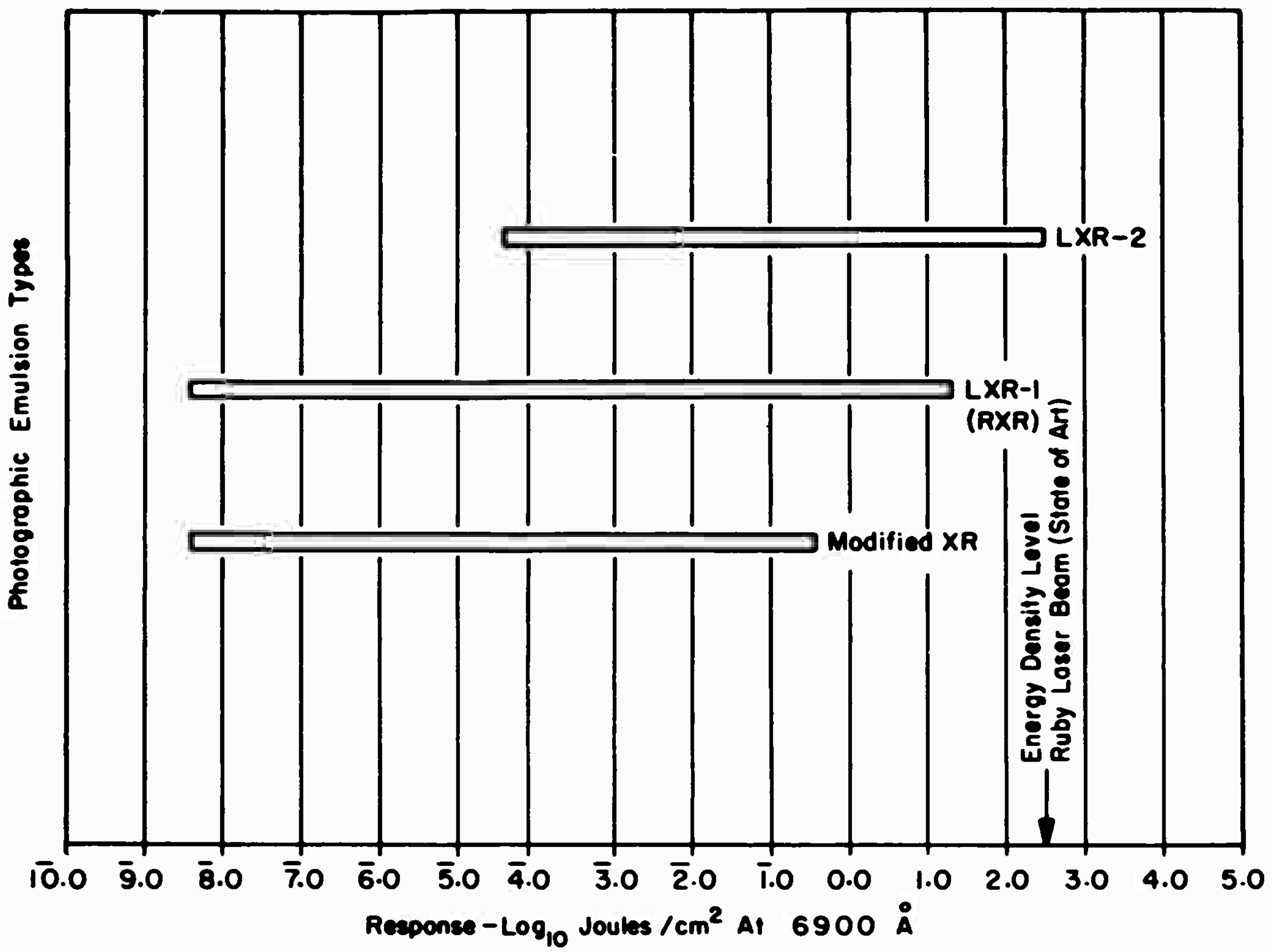

Figure 4 Diagram of energy density response for several proposed photographic emulsions intended specifically for ruby laser-beam studies.

Attainment of this objective, which is a completely new film, would be more difficult to accomplish than the first objective. The type of photographic emulsion that EG&G, Inc. proposed to use was to be composed of exceedingly small crystals of silver halide. The small crystalline dimensions would make the emulsion nearly transparent to visible radiation. Being transparent, this special emulsion was also to be much less sensitive to light than more conventional photographic films. Emulsions of this type, known as Lippmann emulsions, are generally not optically sensitized and maintain only their primitive sensitivity to ultraviolet and visible blue light as shown in Figure 1. In addition, with a more or less uniformly small crystal size, such emulsions tend to have a narrow exposure latitude.

EG&G, Inc. proposed to conduct research to determine whether or not a satisfactory method could be found for optically sensitizing these very minute silver halide crystals which would result in a nearly transparent photographic emulsion exhibiting good response at wavelengths in the near infrared around 7500Å. Being nearly transparent, such an emulsion would possess greater tolerance of energy density without being destroyed. Less optical filtration would be required in the recording path, and the resulting images would suffer less degradation of detail.

Emulsions containing silver halide crystals that are essentially all the same size tend to have a short range of exposure response. Because the emulsion type proposed would consist of these crystals, it was further proposed that the photosensitive materials be made in multiple layers. The various layers of similar emulsions were to have been adjusted in effective photographic speed by means of partially reflecting filter interlayers. These reflecting filters were to function in the same manner as pellicle mirrors, except that they would be an integral part of the photographic film. During the processing of the film after exposure, these reflecting filters were to be removed by chemical means.

To achieve a wide dynamic range of exposures without producing excessively high density, it was proposed that color-forming couplers be incorporated with the various emulsion layers during manufacture. This is, of course, the principle upon which XR film is predicated, thus permitting a total exposure scale of greater than eight decades. However, because the emulsion characteristics of this proposed laser film are considerably different from the more conventional pictorial type emulsions, practical considerations could limit the total exposure scale to a shorter range. Without previous experimental verification, it was difficult to predict the total exposure range.

The third objective of this proposal was an investigation of the use of far infrared energy for producing a usable image with photochromic materials.

Photochromics, originally developed as ultraviolet recording materials, are spiropyrans, triarylmathanes, lactones, benzypyridines, anils, etc., which may be dispersed in a suitable plastic binder which upon exposure produces a visible image. Upon standing, or heating, or exposure to suitable visible or infrared wavelength, the images are bleached to the original colorless state. Either state may be stabilized by suitable chemical means. These properties are the basis of the photographic capabilities of the film. It seemed possible that by reversing the normal photochromic photographic process, a means of recording laser radiation (particularly in the 1 to 10μ region) would result. The film would be pre-exposed to ultraviolet energy and then upon exposure to infrared radiation the absorbed energy would heat the film and selectively bleach the irradiated areas.

Certain experiments conducted in our laboratories suggested the possibility of a material that would respond to wavelengths considerably longer than a micron. The tests indicated that this material required a high-energy density for a change of state, and might be ideally suited for infrared laser diagnostics in the 1 to 10$\mu$ spectral region. Our data indicated that certain activated photochromic materials could be deactivated by application of the appropriate amount of infrared energy and the appropriate amount of such energy in the 1 to 10$\mu$ spectral region appeared to approach the magnitude of laser energy density levels. Therefore, EG&G, Inc. also proposed an investigation of the parameters of photochromic materials for suitability as recording media in the study of laser emissions.

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Most experimental procedures used in this program consisted of standard practice and are described in detail in the general literature. Pertinent procedures are reviewed in this section, and variations from standard practice are emphasized. Experimental procedures intimately connected with the discussion are described in Section 3.

## Reagents

Unless indicated, commercially available reagents were employed in the program without further purification.

## Chemical Analyses

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, New York and Werby Laboratories, 88 Broad Street, Boston, Massachusetts.

## H and D Characteristics

For the most sensitive films exposures for computing H&D Curves were made using an EG&G Mark VI Xenon Flash Sensitometer and a step tablet consisting of 2 Kodak Photographic step tablets overlapped in registration. The proper exposures and processing conditions for the film were determined by trial. For the slower Lippmann emulsions, the H&D curves were generated using a high intensity xenon arc source and a step tablet. The densities were read using a MacBeth Quantilog Densitometer.

Exposure reciprocity studies of the film were conducted using an EG&G Mark VII Xenon Flash Sensitometer, according to the methods described by Wyckoff.[8]

## Spectral Sensitivity

Spectral sensitivity was determined using a Jarrell-Ash 1.5 meter spectrograph and a tungsten light source operated at 3400°K. A photographic step tablet on glass was placed at the slit of the spectrograph and a plastic wavelength marker was inserted in the focal plane. Second- and higher-order energy was eliminated by the use of Wratten filters, and 90% transmission was accomplished throughout the spectrum. The energy at the film plane was calculated.

## Modulation Transfer Function

Modulation transfer functions were determined by the use of a Kodak MTF target exposed through a Wratten 29 filter using tungsten light (150 watt) from a Beseler Model 45MCRX enlarger. The film, target, and filter were held to contact by a vacuum frame. The resultant image was read with an Ansco Model 4 Microdensitometer using both filtered and white light. The resultant plots were then reduced using the technique described in Mees and James.[9]

## Acutance

Acutance was determined using a blade edge with the Beseler Model 45MCRX enlarger used for exposure. The technique is described in Mees and James.[10]

None of the films or plates currently employed in laser research has been specifically designed for this application. The inappropriate spectral sensitivity (<6500Å), the short dynamic exposure range, and the inability to withstand high energy densities are the principal defects of these films. As a result, the media and optical techniques used are usually selected as a best compromise and much image detail is lost.

The research program had the following principal objectives:

1. Modified XR (RXR) Film - To modify the wide dynamic range XR film by extending the spectral response of all photosensitive elements of the film to have a response peak at 6900Å or greater. In addition, attempts were to be made to create a more uniform spectral response in the slow element than the current XR film exhibited.

2. LXR-1 Films - To perform laboratory experiments to determine the feasibility of producing a new film incorporating very small crystal size transparent Lippmann-type photographic emulsions having greater tolerance for energy density, and which would peak in response at 7500Å.

To produce prototype reflecting and partially transmitting silver filters for adjusting the effective speed of the various emulsions, and to include color-forming couplers with the various emulsion layers either during manufacture or during processing in order to achieve an exposure latitude of wide dynamic range.

3. LXR-2 Films - To perform laboratory experiments using photochromic materials to determine the feasibility of recording a photographic image by means of far infrared (1 to 10$\mu$) laser emission. Also included in the task was a study of the environmental factors that influence the stability of the resulting image.

## Modified XR (RXR) Film

In the most recent production lots of XR film, Kodak has provided extended red spectral sensitivity in the high speed emulsion component. Based on the apparent success of this change, EG&G, as the first objective of this program, proposed to supply the contracting agency with an experimental XR film with extended red sensitivity in all three emulsion components. Such a film, designated Modified XR or RXR, with panchromatic response in all three layers, would provide improved recording capability for all ultraviolet and visible lasers. This objective has been completely realized.

A factory experiment lot of Modified XR was received and evaluated (Figure 5). The most sensitive layer was found to be ~0.4 log E faster in white light response (the speed measured at 0.1 above fog) than the equivalent layer in normal XR film (Appendix A), and only 0.10 log E less sensitive to white light than Kodak Royal X Pan which is the fastest generally-marketed film. The medium speed and slow speed emulsions of the factory experiment Modified XR have been found to be approximately equal to the comparable layers in normal XR. All three layers have been successfully spectrally sensitized to provide an extended red peak response near 6900 Å (Figures 6 to 8). These desired combinations had not been previously realized.

Root mean square granularity and modulation transfer data indicated that a marked improvement in grain structure had also been obtained in comparison to earlier XR film (Figures 9 to 12). In addition, the order of the dye couplers within the emulsion layers of this film was changed to facilitate visual inspection of the finished dye images.

The prototype Modified XR film was tested for reciprocity law failure characteristics (Figures 13 to 14). A series of sensitometric scales was exposed at $10^{-2}$, $10^{-3}$, $10^{-5}$ and $10^{-6}$ second using an EG&G, Inc. Mark VII xenon flash sensitometer. The films were processed together by normal C-22

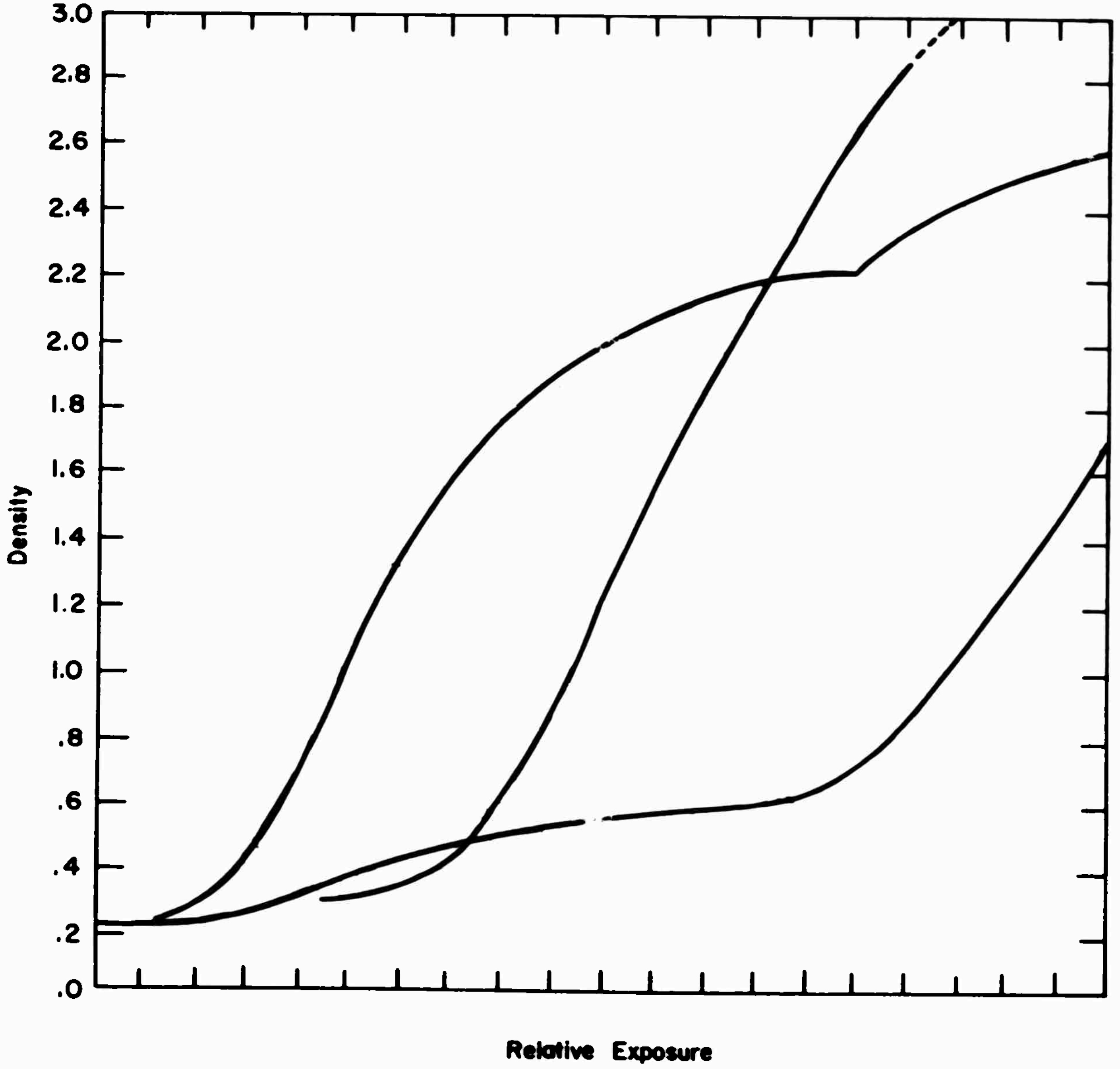


Figure 5. H&D curves for RXR film.

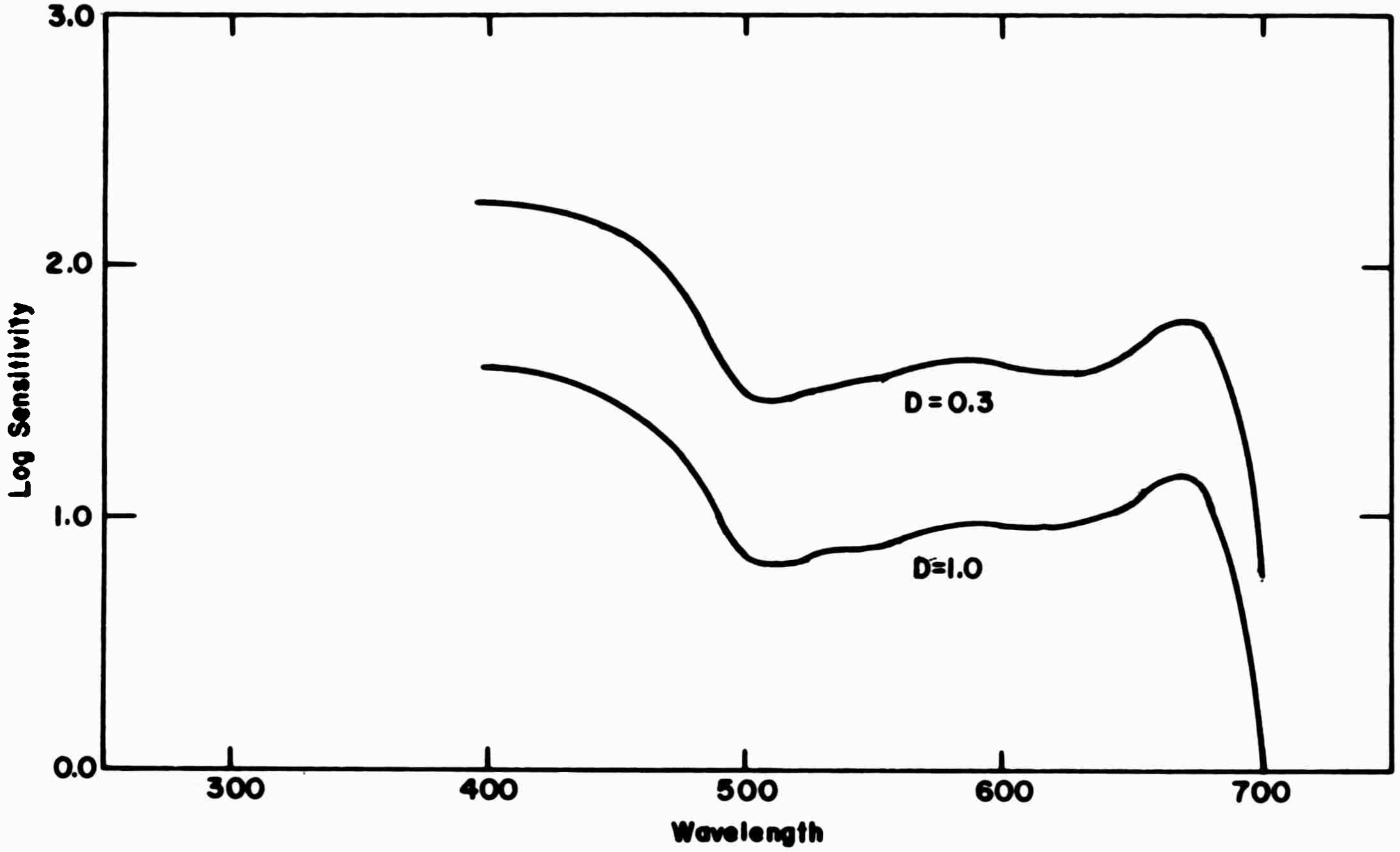


Figure 6. Spectral sensitivity of high speed layer of RXR film.

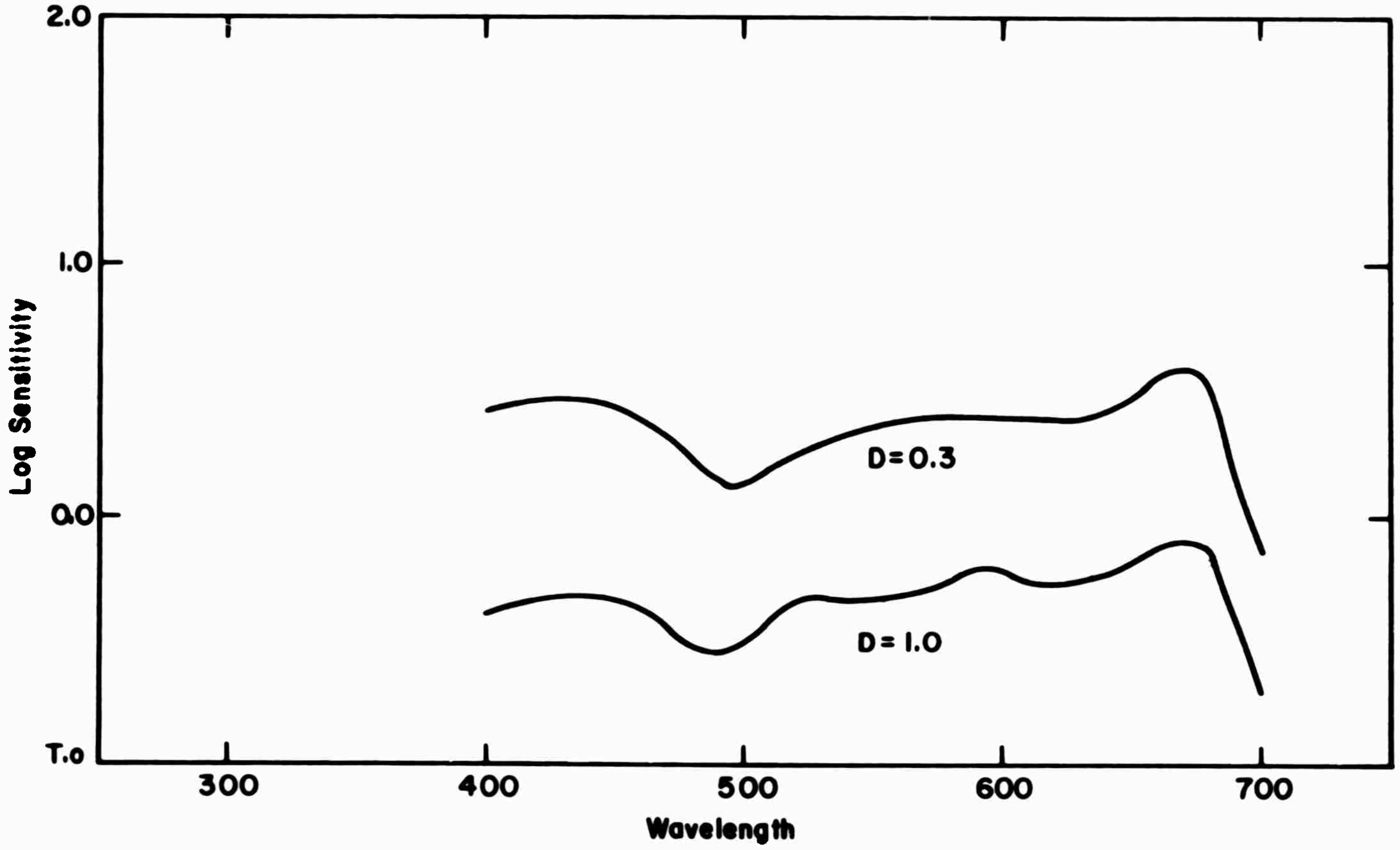


Figure 7. Spectral sensitivity of medium speed layer of RXR film.

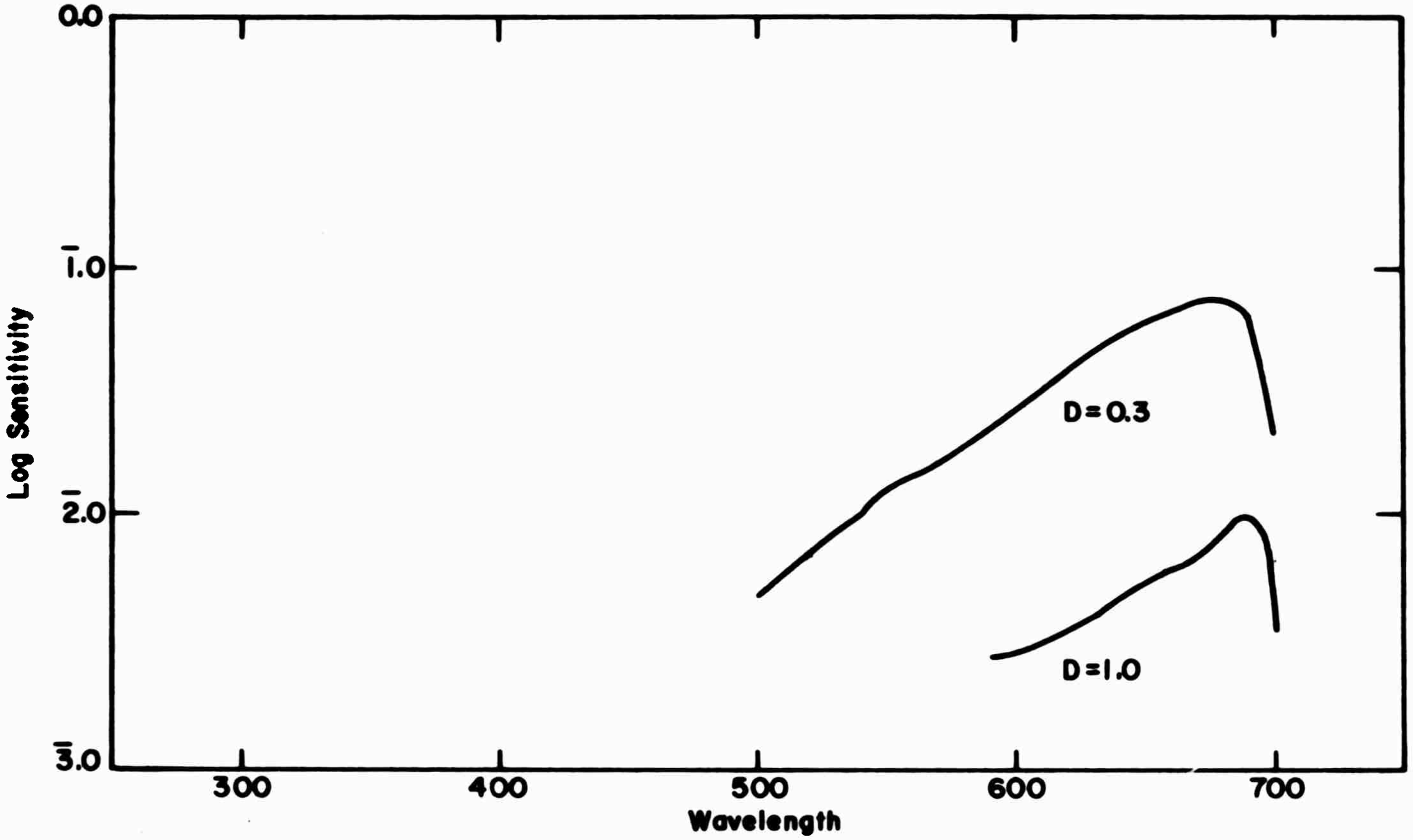


Figure 8. Spectral sensitivity of low speed layer of RXR film.

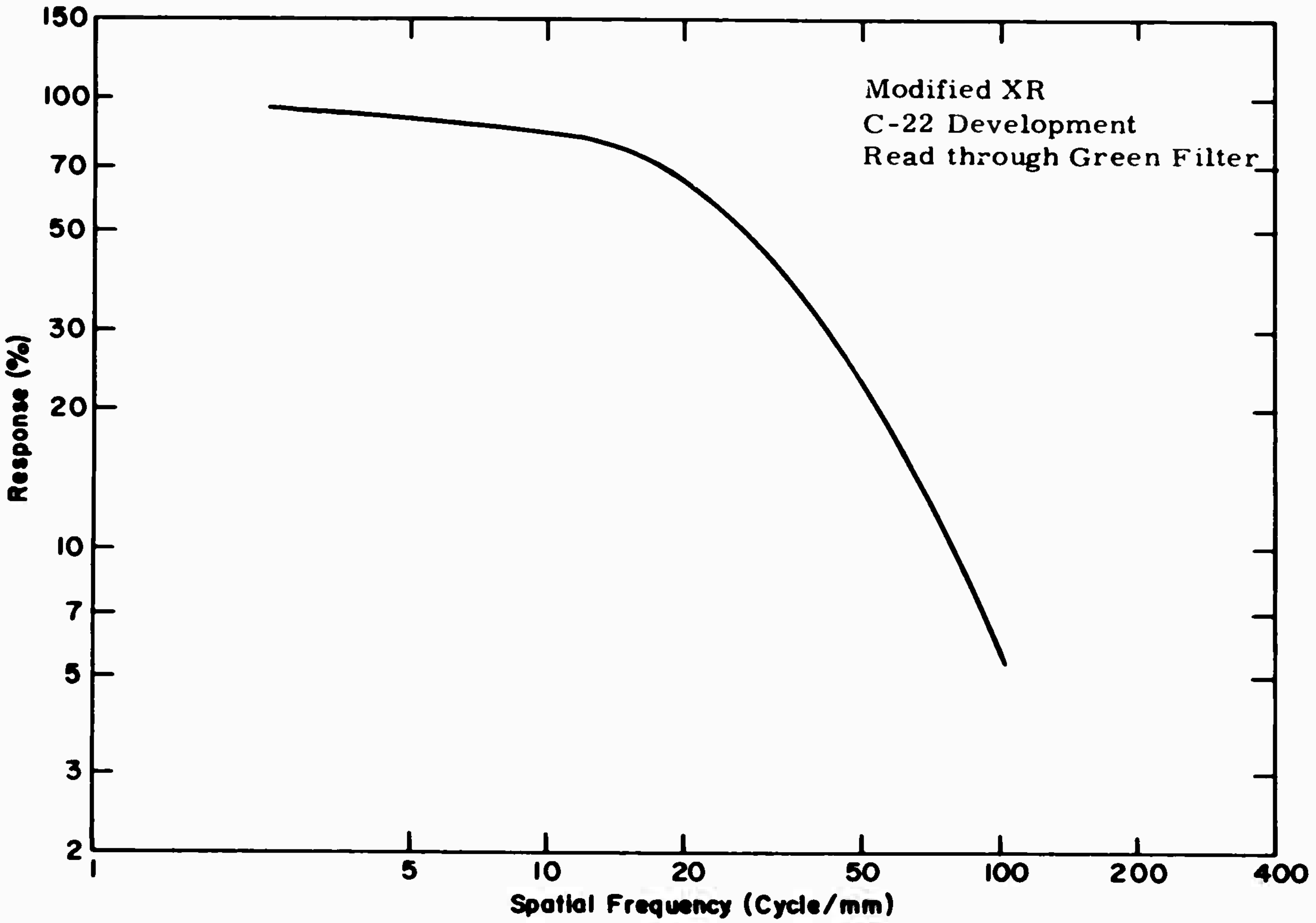


Figure 9. Modulation transfer function of high speed layer of RXR film.

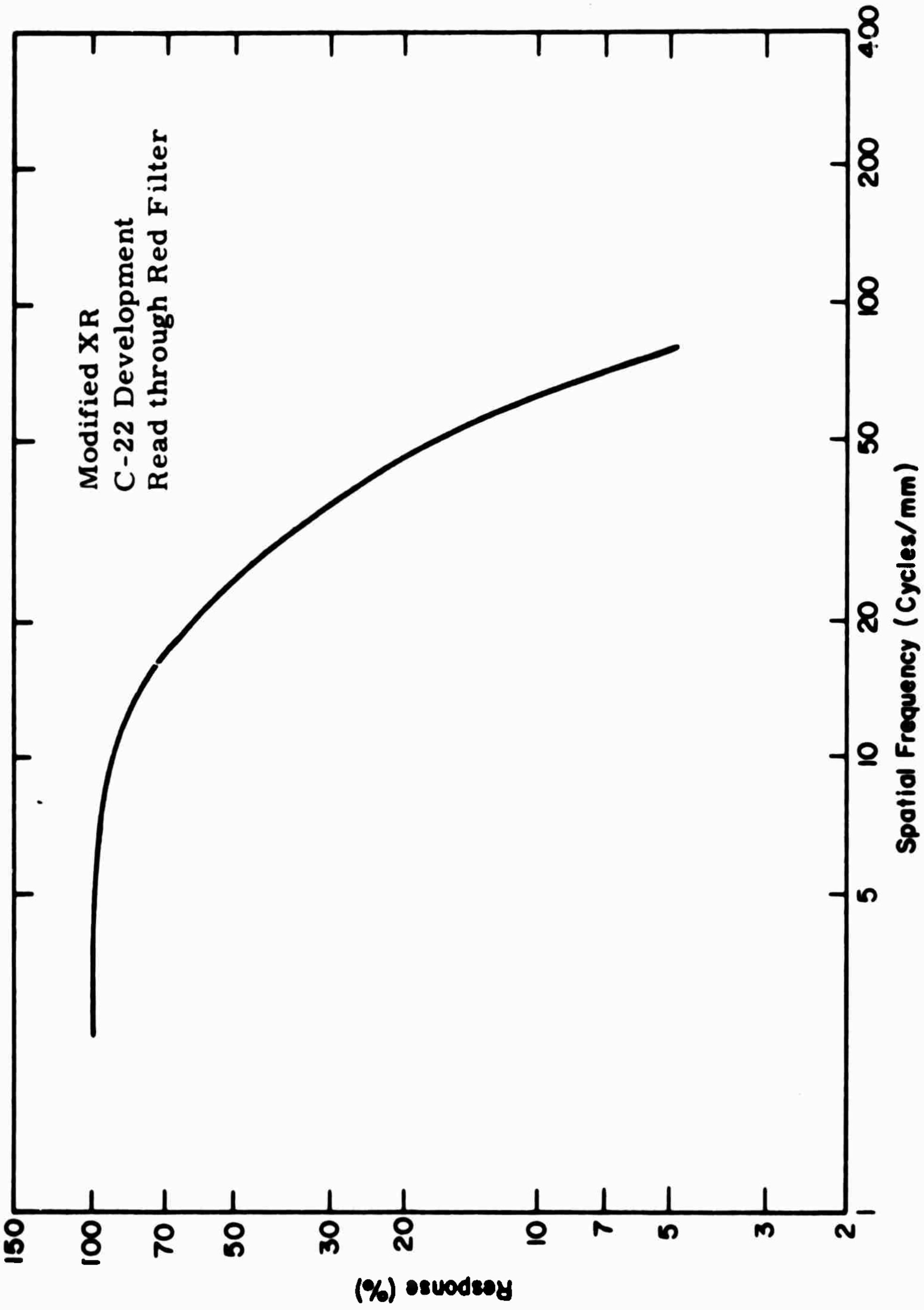


Figure 10. Modulation transfer function of medium speed layer of RXR film.

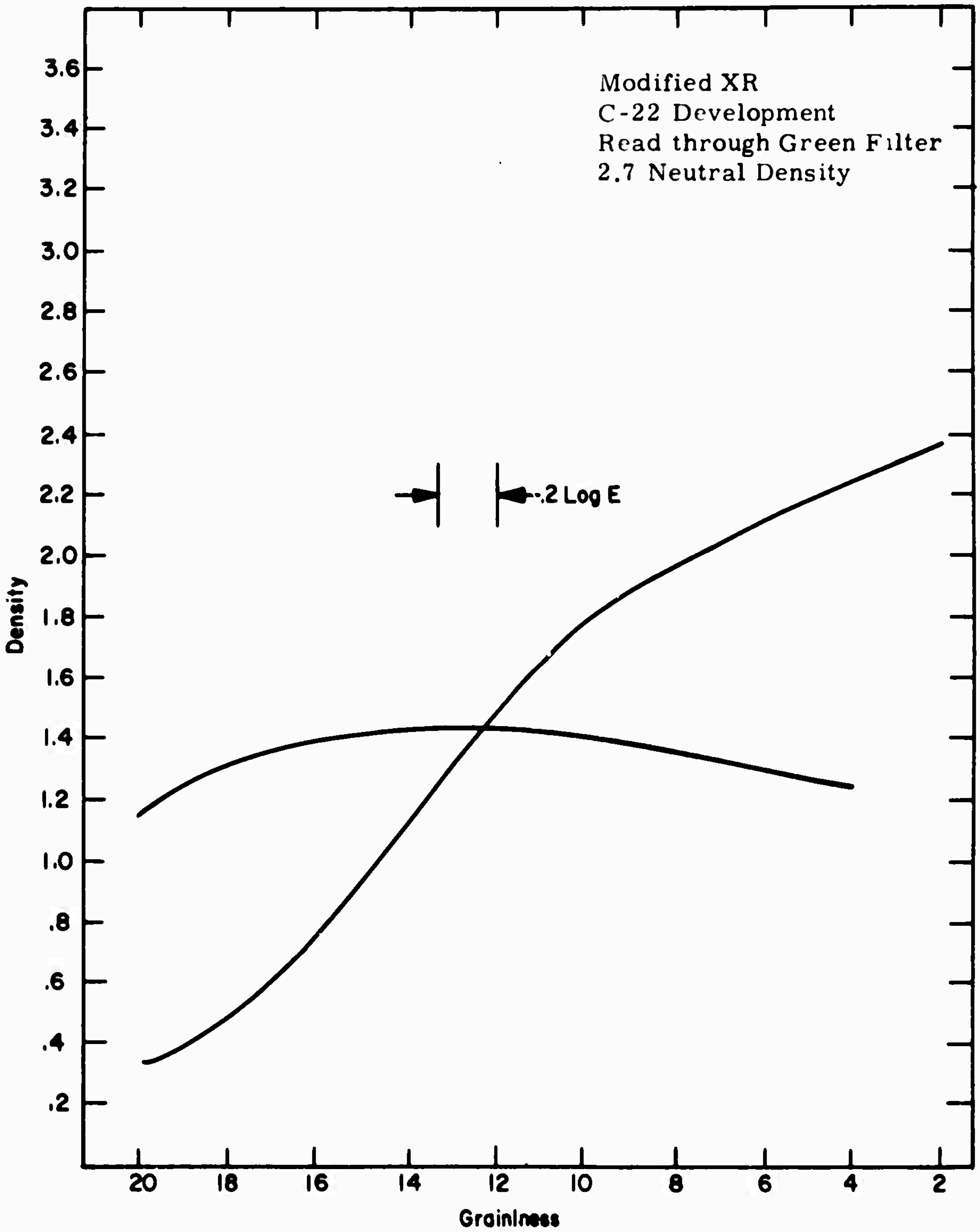


Figure 11. Root mean square granularity of high speed layer of RXR film.

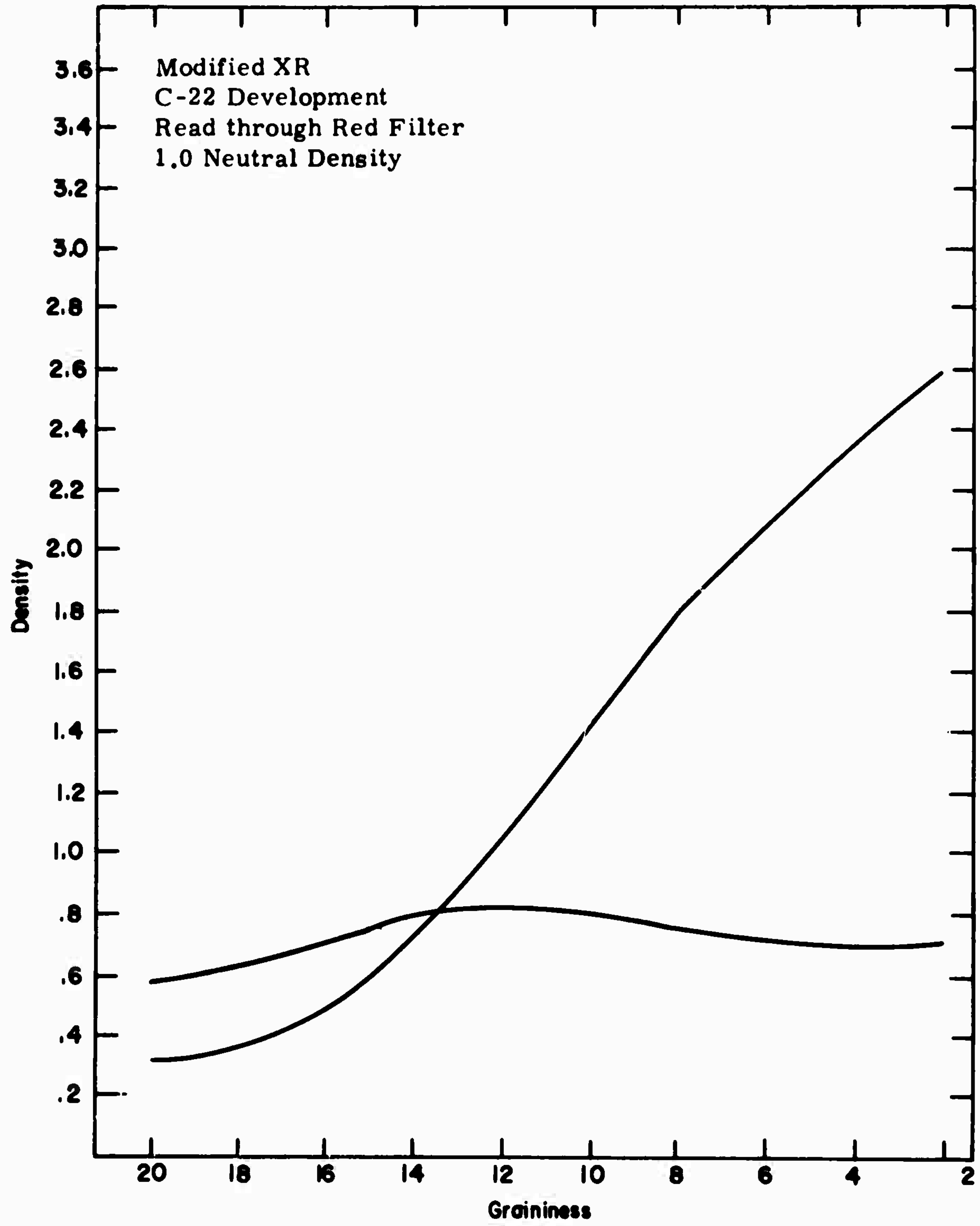
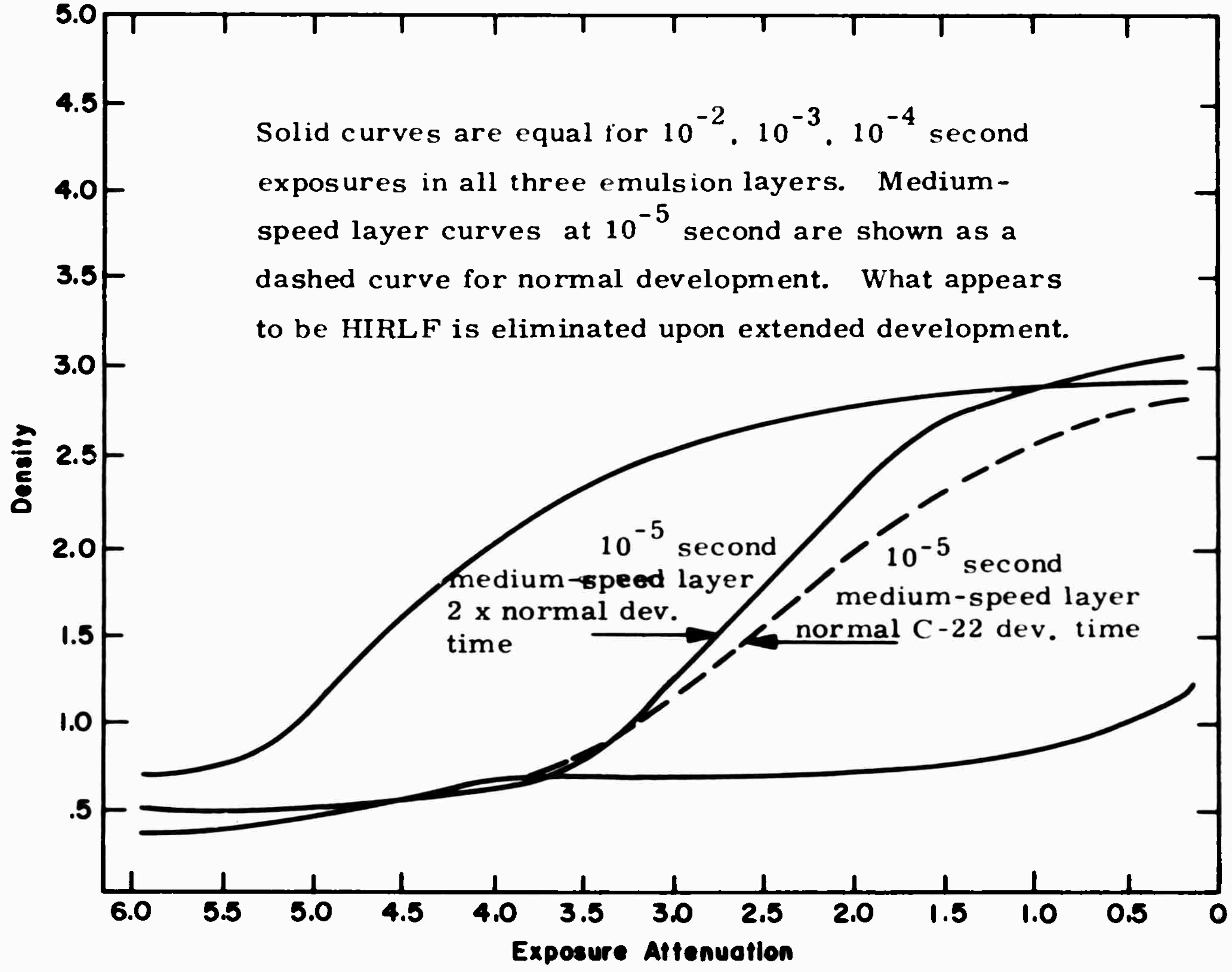
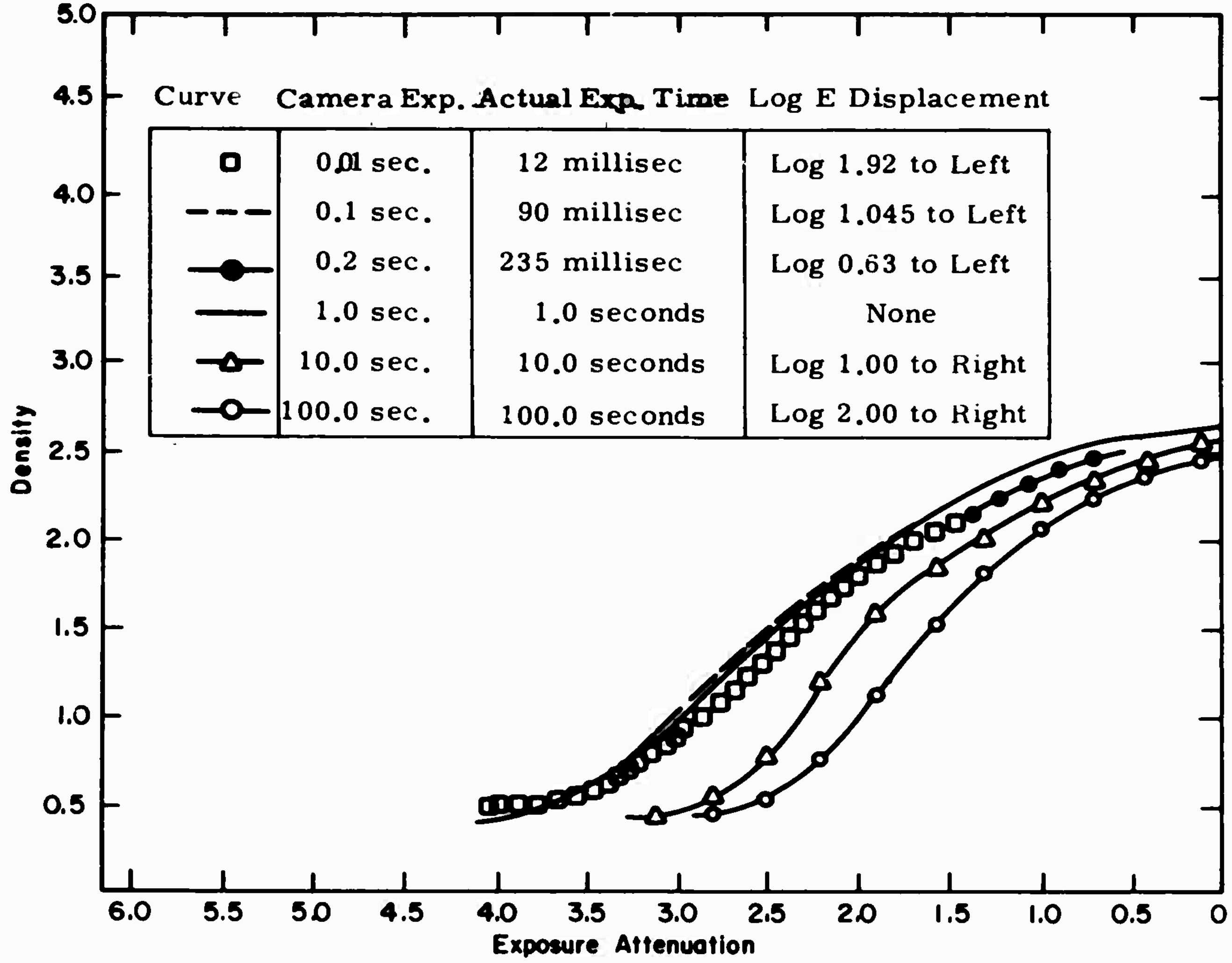


Figure 12. Root mean square granularity of medium speed layer of RXR film.



Solid curves are equal for $10^{-2}$, $10^{-3}$, $10^{-4}$ second exposures in all three emulsion layers. Medium-speed layer curves at $10^{-5}$ second are shown as a dashed curve for normal development. What appears to be HIRLF is eliminated upon extended development.

Figure 13. High intensity reciprocity law failure study of RXR film.



| Curve | Camera Exp. | Actual Exp. Time | Log E Displacement |
|---|---|---|---|
| □ | 0.01 sec. | 12 millisec | Log 1.92 to Left |
| – – – | 0.1 sec. | 90 millisec | Log 1.045 to Left |
| —●— | 0.2 sec. | 235 millisec | Log 0.63 to Left |
| —— | 1.0 sec. | 1.0 seconds | None |
| —△— | 10.0 sec. | 10.0 seconds | Log 1.00 to Right |
| —○— | 100.0 sec. | 100.0 seconds | Log 2.00 to Right |

Figure 14. Low intensity reciprocity law failure study (high speed layer curves only) of RXR film.

chemistry. There was no evidence of high intensity reciprocity law failure (HIRLF) in exposures from $10^{-2}$ second through $10^{-4}$ second in either the fast or medium speed emulsion layers. At $10^{-5}$ second, HIRLF was apparent in the medium speed layer (and probably the slow layer, too). The HIRLF was evidenced by a drop in the average gamma with no loss of toe speed. The contrast of the medium speed layer dropped from a normal 1.0 gamma to approximately 0.85 gamma for equal toe speed (measured at 0.1 above fog). The same result was observed in the $10^{-6}$ second exposure test.

In the HIRLF exposure series, the lack of HIRLF in the fast layer curves may be explained by the fact that it is generally eliminated when a given film emulsion is processed to completion. Such is the case in the processing of XR film by C-22 chemistry. The anomalous behavior of the medium speed layer (and probably the slower layer, also) is undoubtedly due to incomplete diffusion of the developer through the emulsion layers. To prove this an extended development test was conducted, using the prototype Modified XR film exposed at $10^{-2}$, $10^{-5}$ and $10^{-6}$ second on the xenon flash sensitometer. These films were developed for twice the recommended time. H&D curves generated by this test showed that all evidence of HIRLF had disappeared.

A second series of sensitometric strips was exposed to evaluate the low intensity reciprocity law failure characteristics of the prototype Modified XR film. This series was exposed at 0.1, 0.2, 10 and 100 seconds. (Modified XR film strips were placed in contact with a step wedge having a density range of 6 decades, and this sandwich was placed in a film holder for exposure to a uniformly illuminated white card, using a Speed Graphic camera.) These strips were processed together by normal

C-22 chemistry. The resultant H&D curves were carefully matched, and no evidence of LIRLF was noted from 0.1 second to 1 second. At 10 second exposure time, a complete shift was seen. The entire curve had shifted ~0.4 log E to the right for approximately equal gamma. The 100 second curve resulted in a total loss of ~0.7 log E with no loss of contrast. These results were predictable, yet the degree of LIRLF evidenced in the prototype Modified XR film is considerably lower than earlier XR type films.

Modified XR film may be printed over its entire useful range using Kodabromide enlarging paper. This is a great advantage over the older technique requiring panchromatic paper, because normal printing darkroom safelights may be used.

If the original exposures on Modified XR are in the index range from 1200 to 100, prints may be made using a Wratten 9 filter in the optical path. The negatives will appear to be primarily magenta in color. When the image color becomes bluish in the exposure index range from 100 to 10, the printing filter must be changed to a Wratten 58 green filter. By eye, the contrast of the image will still appear to be normal.

When the visual contrast of the XR image becomes noticably flat, it is an indication that the original exposures were in the index range from 10 to 1. Using Kodabromide enlarging paper, this range of XR exposures will require use of near ultraviolet light for printing. Most enlargers emit some ultraviolet of the required wavelength, and with the proper ultraviolet filter placed over the lens, satisfactory prints can be made. However, it has been found more expedient to use a light source which is rich in ultraviolet, such as an argon lamp of the type used in aerial contact printers.

Use of ultraviolet for enlarging XR negatives demands that image focusing and alignment be accomplished with visible light. After such focus and alignment, the visible light must be turned off and the exposure made with the ultraviolet source alone.

XR negatives exposed in the index range from 1 to the limit of the film (0. 001) can be enlarged using the normal tungsten enlarger light without filtration. The visual contrast of the negative will appear to be normal.

Contrast of the print may be varied by using different contrast grades of Kodabromide printing paper. For example, it has been found that, in most cases, the normal grade 2 paper produces excellent results. However, those prints made with ultraviolet light will probably require paper with greater contrast than normal grade 2 paper will provide.

Exposure times of 10 to 100 seconds while enlarging a 35 mm negative to 5 inches x 7 inches appear to be in the operating range at f/4. 5. Some enlargers may require more time while others will need less, depending upon the light source and lens system.

## LXF-1 Films

The second objective of the program was the development of a completely new multilayered photographic film based on Lippmann emulsions with partially reflecting mirror interlayers. The optimum design would result in a film completely transparent except for the mirror component. It would also have a uniform spectral response into the infrared and exhibit an exposure latitude of several, possibly nine, orders of magnitude. The transparency and spectral response would be gained by the proper choice of emulsion constituents. To obtain the required exposure latitude, a multilayer film must incorporate different color couplers into the layers to provide information separation. This objective is then essentially the fabrication of a newly designed color film.

To design a film capable of recording at the energy levels of present high power lasers, and to provide the film with wide latitude and spectral response into the infrared have required the use of the most advanced emulsion and film technology. During the second phase of this program a wide variety of specialized photographic emulsions were investigated for the purpose of producing a silver halide film for recording the output of high energy lasers. As a result of this direct approach, a number of decisions were made based on the interpretation of limited data, and many emulsion formulation questions were left unanswered.

The work conducted can be placed in the following five categories: 1. film design, 2. silver halide emulsion formulation, 3. spectral sensitization, 4. photographic color formation and 5. emulsion coating. Most of the research conducted in each one of these areas was to a large degree dictated by the results obtained in another area. The complex interactions resulting from the combined considerations of each area accounted for most of the problems to be overcome in order to produce LXR-10, the final and most successful film.

In the original design, the film was to be a highly transparent multilayer silver halide material incorporating XR principles. The high-speed layer was to have a speed of ASA 400 and the film an exposure latitude of $10^{12}$. After initial experimentation with Modified XR and Kodak Fine Grain Positive (a non-spectrally sensitized printing film) in recording a helium-neon and pulsed ruby laser (see Figure 15), it became apparent that maximum speeds of ASA 1 were adequate for all lasers of present research interest. The prime design criteria was the transparency of the emulsions in the 0.6 to 1.0 micron spectral region in order to tolerate, undestroyed, the high energy densities to be encountered and which in combination, in multilayer film designs, would possess the latitude in photographic properties which would allow the recording of laser emissions in exacting detail.

The preparation of photographic emulsions is a critical process whose reproducibility and results depend on many factors. To this end, a variety of emulsions offering broad ranges of photographic properties have been studied in some detail. Efforts have been directed toward tailoring and trimming the properties of these emulsions through modification of such factors as silver halide to gelatin ratio; rates, agitation and temperature at precipitation; gold and dye sensitization; and subsequent temperature histories. A considerable body of information has been developed regarding speed, gamma, $D_{max}$, fog, granularity and MTF values for the formulations described in Appendix B, both as black and white and color emulsions.

Three general types of emulsions were to be developed for the LXR-1 model films: high speed emulsions which were to be at least ASA 400, medium speed emulsions of ASA 2-10 and slow Lippmann emulsions of ASA 0.001. The initial work was undertaken to produce the high speed emulsions since this is generally a difficult area and the application is complicated by the requirement of high transparency. Three approaches became apparent regarding the latter requirement. One was to make the emulsion layers as thin as possible consistent with the desired photographic properties. Another was to design smaller silver halide crystals with higher sensitivity, and the third was to develop methods of utilizing less silver metal to produce the desired image densities. Transparency was not originally a consideration in the high speed emulsion research, however, as gaining ASA 400 posed difficulties in itself. Work subsequently would be performed to obtain transparency by the above approaches once this sensitivity level was obtained.

Many emulsion formulas labelled high speed in the photographic literature are actually medium speed by present standards. The most promising of these formulations were tried. Most of them gave speeds of about ASA 10, and would not easily go much above this sensitivity. Two emulsions did show promise in giving the speed desired for the high speed layer. One was a precipitated boiling emulsion made by Alantic Gelatin Corporation and known as E-13. The other was described in a formula published by B. H. Carroll (see Appendix B) at the Rochester Institute of Technology.

With proper modification of these emulsions, primarily by an increase in the precipitation temperature from 140 to 160°F, speeds of approximately 400 were obtained. Work on these emulsions was not yet complete when it was discovered that it would not be necessary to use emulsions having this speed.

Experience gained while working with the high speed emulsions contributed to solving the problems relating to the development of LXR-1 films from the outset. Since the original film design required a wide variety of emulsions, it was necessary to compromise on the gelatin selected for the film. It was highly desirable that the same gelatin be used for all emulsions because the use of different gelatins would have required extensive research into gelatin additives.

After discussion with manufacturers, it was decided that a semi-inert gelatin manufactured by Alantic Gelatin would be best for our general purposes, considering the wide range of emulsions that were needed. The gelatin selected proved to be acceptable, but later experiments indicated that it was easier to produce medium speed emulsions than it was to produce other emulsions.

Work with the high speed emulsions gave insight also into the problems associated with removing soluble salts formed during the silver halide precipitation. It was found that washing strongly influenced the characteristics of the final emulsion and usually increased the film speed and transparency. An excess of bromide, potassium, or sodium ions in an emulsion is usually detrimental to its speed and physical characteristics. Thus, efficient washing is essential, as it will provide a higher speed for any given grain size.

Two methods of washing are generally used. They are referred to as noodling and gelatin precipitation. The noodling method is the simplest but proved to be the least effective and controllable. Noodling consists of cutting the emulsion into small pieces, and then extracting it continuously with cold water. Washing after gelatin precipitation is a much more efficient method.

The three main reagents used to initiate the coagulation of the gelatin are sodium sulfate, zirconium sulfate, and methanol. Initially, all of the above coagulants caused problems which were not at first readily predictable; each formulation seemed to require its own washing procedure and did not work properly when other procedures were used. The quality of the precipitates caused by sodium sulfate and methanol never appeared to be good, even for emulsion formulas which were designed for them. They always seemed to form a large congealed mass that was difficult to work with and get back into solution.

In some formulations zirconium sulfate gave a fine but very heavy precipitate that was easy to wash, and easy to get back into solution. It too, however, was prone to form a heavy mass and to prevent precipitation in certain formulations. It was subsequently discovered that the concentration of both the gelatin and silver halide was extremely important in determining the quality of precipitate. Generally, a gelatin concentration of less than 0.1% was necessary to yield good precipitation. A higher concentration of gelatin could be used if the silver halide concentration was also very high, but this resulted in the formation of large silver halide grains.

A low gelatin concentration also resulted in many other problems, some of which made precipitation impractical for some formulations. It was discovered that it was possible to dilute emulsions before precipitation of the gelatin with no apparent adverse effects as long as the temperature remained below $90^{\circ}$F.

Very little work was done on medium speed emulsions since they possessed optical density characteristics similar to the high speed emulsions which were destroyed by high energy laser emissions.

Much of the work was directed toward preparing very fine grain Lippmann emulsions. Lippmann color-forming emulsions have been prepared, possibly for the first time. The high color production in these emulsions is notable. Dye sensitization is readily achieved, though it is more difficult to control than in standard emulsions. Spectral sensitization has been extended to beyond $1\mu$ through the use of infrared sensitizing dyes prepared in our laboratories. No particular difficulty has been caused by the interaction of sensitizing dyes and color couplers provided the dyes are added to the emulsion prior to the addition of the color couplers. Some work with patented procedures indicates that couplers may be incorporated into films in separate layers in those cases where interference occurs. Since the silver halide and coupler are no longer in the same layer, development must occur through oxidation product diffusion with a resulting loss in film resolution.

Very highly transparent (optical density 0.01 to 0.1 to red light) emulsion coatings have been prepared with effective photographic speeds ranging from ASA 10 to $10^{-8}$ through low temperature precipitations at high agitation rates. It was originally thought that Lippmann emulsions were not capable of giving wide exposure latitude, but by control of precipitation and constituents it is possible to prepare emulsions having an exposure latitude of greater than $10^{6}$ with a gamma 1.0.

Two particularly significant developments occurred. The slightly high fog levels previously reported in the case of the high speed precipitated boiling emulsions were reduced to acceptable levels. This was done by experimenting with digestion procedures when the use of antifoggants, such as 6-nitrobenzothiazole, did not provide satisfactory control of fog. Overcoating emulsion layers with a standard intercoat formulation of 5% gelatin with formalin and gum arabic also resulted in diminished fog levels without loss of photographic speed.

Experiments with silver content to improve the dye yield in slow Lippmann emulsions when used as the bottom layer in an XR film has led to the development of a transparent emulsion with an ASA speed of ~200. This emulsion appears to have an exceptionally high speed-times-resolution figure of merit, and should be subjected to extensive examination. The instability of this emulsion and lack of reproducibility have not been resolved.

Increasing the silver content of the emulsions to provide higher image densities without increasing the emulsion speed has been the subject of much study. It has been possible to accomplish this by minimizing the water content of the gelatin when attempts to increase the silver loading of the emulsion were unsuccessful. By means of proper digestion and sulfide sensitization, controlled fine-grain emulsions of ASA 20 were prepared in studies to formulate high speed transparent emulsions. Gold sensitization has not been effective. Very slow addition of silver ions has been used to gain speed increases while maintaining transparency. However, this produces some loss in gamma.

During the course of these efforts, it became possible to prepare emulsions over the entire sensitivity range of ASA 0.0001 to ASA 10 with exposure latitudes of five to six orders of magnitude. Such emulsions enable the preparation of single layer, wide dynamic range film without color couplers. They may also result in further increases in film transparency; and when used in multi-layer structures with couplers, they may increase the dynamic range of the film.

Ultra-fine particle size and high silver surface activity introduce emulsion technology considerations which are specific to Lippmann emulsions. Also, in emulsion experimentation, the Lippmann emulsions introduce some practical considerations which are not otherwise encountered, such as very long exposure times to gain evaluations, temperature control to prevent grain growth, etc. Therefore, it was deemed advisable to perform much of the developmental trials on more normal emulsions. In doing so, it has become apparent that EG&G would be able to deliver several LXR-1 films, based on both the Lippmann emulsions and on more conventional types. Although the latter film would probably not possess the speed values in the fast layer which RXR has, advantages in other characteristics will be described.

The starting point of the Lippmann emulsion research was to find a published formula which could be easily adapted to the criteria set by the design of the LXR-1 film, yet allow for experimentation to obtain improvements. Different combinations of halides and methods of precipitation were used. A bromo-iodide emulsion was finally chosen (Appendix B) because it offered the highest initial speed and greatest transparency.

The effect of the iodide concentration immediately became of interest in that increased iodide gave higher speeds (though processing times became considerably longer) as well as higher transparencies. Concentrations of 100 and 1000 times the amounts in the original formula gave speeds that approached ASA 1 before digestion.

The addition of iodide to any silver halide emulsion is known to effect increases in speed. The Gurney-Mott silver halide latent image theory proposes that it forms imperfections in the crystal which are used as image sites. It is also known that too much iodide generally slows down the emulsion, even to a greater degree than the emulsion without any iodide. In our experiments however, speed increases were obtained even when using 100 times the amounts of iodide that are considered optimum on a molar percent basis in normal emulsion work. However, a yellow dichroic fog, characteristic of these emulsions, made them impractical for our use.

Our fastest Lippmann emulsions were obtained using potassium iodide concentrations that were 100 times greater than those used in the original formula. These emulsions developed in 10 minutes in D-76 at 75°F. They did not, however, attain the high gamma values of typical Lippmann emulsions; 0. 5 was about the highest attained.

When using concentrations of 1000 times the amount used in the original formula,development times became longer than 1 hour, and there appeared to be a further speed increase, though the gamma was so low that it was difficult to get an actual speed reading. These very high iodide emulsions showed some interesting results in that they could be developed in highly active reducing agents that would cause other films to fog. D-76 at a pH modified to 12. 0 and a temperature of 80°F for one hour did not seem to overdevelop the image, and gave no real change in the final image other than the low gamma found in the more normal development reported earlier. The gamma was too low for useful density measurements.

The addition of sodium thiosulfate to the D-76 developer (10g. /liter) resulted in higher gamma and speed, and a rise in the fog level.

Because of compatibility problems with other emulsions that have the correct characteristics, the iodide experiments were terminated. However, these emulsions show great promise in producing the very high speed, high transparancy emulsions that are desired in laser recording work. The use of development accelerators, anti-foggents, and silver halide solvents, may make these high iodide emulsions useable in a multilayer film using more conventional emulsion technology.

A limited amount of research was done on straight silver iodide emulsions, which while very transparent to red light are also very slow. The emulsions proved to be too slow to record 5 joule/cm$^2$ laser emissions. Films intended for use in the highest powered lasers, however, may make work in silver iodide emulsions necessary. As it appears from the work done, straight silver iodide emulsions can be made which are at least five orders of magnitude slower than the slowest emulsions which are obtainable using other halides. They are readily dye sensitized. The halide itself appears to have very little optical density in the red region of the spectrum. Even thick coatings have densities less than 0. 01 although the emulsions appear visually bright yellow when viewed in white light.

Emulsions were also made without any iodine, using the standard Lippmann formulation. These emulsions retained similar gamma characteristics, but were 10 to 100 times slower than the same emulsion made with the addition of potassium iodide. Optical clarity was essentially the same for both the iodide and non-iodide emulsions before digestion took place. The non-iodide emulsions digested slower than those with iodide.

The maximum speed which could be obtained upon digestion was very close in both types of emulsions. The non-iodide emulsions showed more optical density when digested fully. The development rates of the two emulsions were highly dependent on the concentration of iodide, as indicated previously. This became a very serious problem when the films were finally made, and required compensation in development time to obtain usable results.

One of the more difficult problems was that of obtaining a higher silver concentration in the gelatin. The standard Lippmann formula as given in the literature had a high gelatin concentration in comparison to the silver. This presented many problems, and rather extensive work was conducted to try to obtain a greater amount of silver halide to a given amount of gelatin for the following reasons. For the silver content specified, rather thick coatings were necessary in order to obtain reasonable image optical density. This was undesirable in a multilayer film as total thickness became too great for practical coating on a flexible support. Difficulties were next encountered with color couplers when using high gelatin concentration. The long chain couplers finally used greatly altered the characteristics of the gelatin, and these characteristics could be better controlled in emulsions having a lower concentration of gelatin. The high gelatin concentration affected the hardening of the emulsion, which is an important consideration in emulsion coating, and subsequent processing and image stability.

The most obvious change would be to decrease the gelatin in the formulation, while holding the remaining constituents the same. This was done several times with modifications but did not yield useful emulsions. These emulsions were always too fast, and were very milky relative to their speed. They were also prone to fogging. Lowering the temperature of the precipitation and changing the iodide concentration helped only somewhat. Increasing the silver in a given amount of gelatin, and retaining the desired characteristics of speed and transparency is still a prime concern. Recently some promising emulsions have been made by diluting the gelatin to a lower weight concentration and precipitating at a very low temperature. The best results have been obtained at precipitation temperatures of $80^{o}$ to $90^{o}$F. However, these emulsions have suffered from problems of reproducibility. Literature research has indicated there are some chemical means which may be useful in keeping grain size small in very low gelatin concentrations.

Experiments were also conducted using additions of sodium thiosulfate to the gelatin. The addition of trace amounts of sodium thiosulfate (2 - 5 parts per million) to gelatin increased the initial speed about 100 times. There was a slight increase in the optical density, though not as much as when the same speed was achieved by digestion of a normal Lippmann formula emulsion. However, these emulsions did have a very low gamma, usually 0.3 or lower, and were easily fogged. With the addition of certain restraining agents in careful balance, these emulsions might prove to be very useful for laser recording films because of their high speed and transparency.

When a commercial source of non-diffusing couplers could not be found, and the literature descriptions of their synthesis proved them to be inordinately expensive to make, oil encapsulation of the color couplers was investigated. In this method an organic liquid containing the coupler is physically dispersed in the photographic emulsion by high speed homogenization. The organic liquid is water insoluble but permeable to the developer oxidation products. The technique appears to be equally applicable to all couplers, but the following were used as they showed sufficient coupling efficiency, color value and availability: 2, 4-dichloro-1-naphthol (cyan); 3-methyl-1-phenyl-2-pyrazolin-5-one (magenta); 2, 5-dichloroacetoacetanilide (yellow). The oil used was ethyl phthalate, which was selected on the basis of coupler solubility, index of refraction and physical effects on the emulsion.

Kodak C-22 processing gave high dye yields with $D_{max}$ values of ~2.00 and gammas of 0.50 at 1.5 moles coupler per mole of silver in the high speed emulsion. Microscopic examination of the dye images at 800X proved the dispersions were finer and sharper than that provided by Eastman Kodak in commercial XR film. Effective coupling has also been achieved in the medium speed slow bromide emulsion.

Spectral absorption characteristics of the dyes were determined in ethyl phthalate. This data is required to determine the exact gamma and speed characteristics necessary to produce a balanced film. The yellow dye was found to be very pure, but the cyan and magenta dyes are high in blue and red absorption respectively. The poor quality of these dyes does not cause any printing problems in a film using XR principles, since complete separation is not a requirement. Because of this unwanted absorption, it will be easier to make a film which is easy to print, if this is desired, since all spectral regions will have some printing density.

Investigations with oil encapsulated color couplers as a means of preparing color emulsion continues in order to improve the physical and general photographic properties of the color emulsion layers based on this system. But, while individual emulsions have been developed which are generally satisfactory, considerable difficulty was experienced in attempting to combine them to form a multi-layered XR film. No more than four layers of these emulsions have been successfully coated one one film without loss of adherence to the base. High silver density has not been realized in the lower layers and, despite interlayers, the colors have persisted in bleeding, producing grey tones and virtually no XR properties.

While these problems were being subjected to detailed examination, non-diffusing color couplers (of unstated structures) became unexpectedly available from CIBA Ltd., one of the several firms to which inquiry had been made in this regard. Evaluation of twelve of these in various formulations demonstrated ease of color formation, high dye yield, color purity and total lack of dye diffusion. The color emulsion phase of the program was immediately directed toward the use of these materials.

The use of CIBA dyes also solved the difficulty of increasing image density without increasing speed in the very slow speed emulsions. This eliminated the necessity of multiple coating the same emulsion. Particular dye selection was then based on a compromise of their light absorption characteristics as related to visual observation, printing of the images, and the physical properties of the emulsion formulations.

The extremely narrow spectral output of lasers makes a uniform spectral response very desirable. 3, 3'-diethyl-9-methylthiocarbocyanine bromide generally gives very smooth sensitization from 450 to 650μ and dicyanine A picks up at about 650μ and has sensitivity to 780mμ. Acceptable dye sensitization of each of the emulsions described here has been achieved. When commercially available IR sensitizing dyes proved photographically ineffective, xenocyanine (800-1200 mμ; λ max 980 mμ) and strongly sensitizing dyes of the neopentylenethiatetracarbocyanine class, for example, 3, 3'-diethyl-9-11-neopentylenethiatetracarbocyanine (750-975 mμ; λ max 800, 925 mμ) were prepared. (Appendix C). Although present experimentation with ammonia hypersensitization has proved to be ineffective, the 0.7 to 1μ sensitivity of standard formulations employing these dyes is generally only two orders of magnitude less than the primitive sensitivity of the conventional emulsions, while in the ultrafine grain emulsions it is actually higher.

Several non-sensitive layers have also been developed to perform various functions in films. Reference was made previously to the use of overcoating to diminish fog in fast film layers. Microscopic examination of microtomed cross-sections of several commercial films which employ non-diffusing couplers has revealed the presence of interlayers between each emulsion layer. Undoubtedly they reduce molecular diffusion, particularly of the oxidation by-products generated during processing. Other additives such as developer accelerators might also be present. In our fabrication of multi-layer XR type films, speed losses in a lower layer considerably out of proportion to the optical density of the layer above it are observed. One approach to compensate for this effect is the addition of developers to the adjacent interlayer. Other related techniques to tailor photographic properties, such as the lowering of gammas by use of citrazinic acid, have also been developed.

Hardeners have been found to have a pronounced effect on silver image density in Lippmann emulsions with aging. Slow acting hardeners increase density (and gamma) while more rapid hardeners act in reverse. Since the CIBA couplers also exhibit hardening activity, conventional hardeners are being used at present only in the interlayers, primarily as an aid to reducing diffusion.

The problem associated with development of suitable hardeners is presumably best solved by the addition of 1% volume of a 1% potassium chrome alum solution. Occasionally this causes difficulty through interactions with the couplers, especially if emulsions are allowed to cool at all. The use of formalin also resulted in excellent hardening properties until problems with couplers and emulsion stability appeared that seem to be traced to it. Excellent color layer separation is presently being achieved, although some of the described difficulty caused by the hardeners with the image in the Lippmann emulsion is still present.

The remaining major area of consideration in film production is the coating technology that has been developed to provide emulsion layer thickness from 2 to 25 microns through modification of emulsion viscosity by temperature and alcohol content.

The coating of a uniform layer of emulsion upon a flexible base is one of the most difficult areas in photographic film manufacture. The manufacture of multilayer films became proportionally more involved.

Good coatings of emulsions have been obtained in many cases, but a particular coating technology associated with viscosity, surface tension, foaming and other variables is required for each emulsion. Structurally sound 35 mm fourteen layer films have been produced in several hundred foot lengths. In accomplishing this, several practical technical problems had to be overcome.

The coating machine itself is undergoing design modification and development to meet the demands of the various emulsions under consideration. The machine contains a variable speed film drive and emulsion applicator, and a flexible chilling and drying system. The machine has the flexibility to operate using dip or emulsion transfer coating methods.

A source of suitable film base was a continuing problem during the course of the program. Originally, coatings were made on old film stock which had been cleared. Owing to the possibility of contamination, however, this was used only in trial work. Originally, coatings were made on Eastman Kodak Film Leader No. 4. This base is not subbed, however, and satisfactory methods of providing a reliable subbing were not successfully developed. The use of Celanese subbed film base proved to be more successful and gave very good results. This base, however, is available only in large lots and must be slit, so methods to avoid its use were sought. It was learned that when the CIBA couplers are used in the emulsions, very good adherence to the base also results. At this time no successful way of keeping gelatin emulsions without these couplers in them on the Eastman base has been devised. There are however, several hardeners which cross-link gelatin much the same way that these couplers do, and it appears possible that one of these hardeners coupled with a relatively high pH solution may make a useful subbing for the Eastman leader film.

Problems with coating the emulsions are many, and there are some chemical means to help elevate them. The use of a surface tension relieving agent such as saponin proves to be necessary. One milliliter of a 5% solution of saponin per 100 milliliters of emulsion greatly improves the coating characteristics for any machine configuration. It is the single most important additive that is used in the emulsions under study.

Hardeners are also important for film if it is to be used normally. These are difficult to work with when using CIBA couplers as they cause the emulsion to become viscous and to coat unevenly. Hardeners were finally used only in the intercoat stages of the multilayer films. However, they do improve the characteristics of the emulsion.

Foaming of the emulsion is an ever present problem, especially when the transfer roller technique is used for coating. The use of 1.0 milliliter of benzyl alcohol per 100 milliliter of emulsion reduces foaming to a large extent but it is still a problem. The dip coating method seems to minimize foaming probably because there is less agitation of the emulsion.

The use of gum arabic in an emulsion greatly improves its adhesion properties. Amounts of 1% by weight of the gelatin proved to be the most satisfactory. Gum arabic is used for subbing glass plates, and a coating of high pH gum arabic mixed with gelatin may prove to be a usable subbing for the Eastman leader base.

Control of viscosity is very important especially when making multilayer coatings. Dilution of the emulsion with water as a control has been used successfully. Initial experiments, however, using methanol and ethanol have indicated that these are superior, especially when coating emulsions containing the CIBA couplers.

An aqueous ethylene glycol-glycerin bath has functioned well to reduce film curl and is also worthy of note.

Photographic processing techniques for each emulsion in a multilayer film must also be devised as each layer is applied. Considerable control of observed sensitivity and other properties has been realized in this manner in gaining film of predetermined sensitivity balance. Iodide is used in emulsions to retard development.

The best examples of high speed LXR-1 models were subjected to evaluations as laser recording media. LXR-1C, with speeds of ASA 50, 1 and immeasurably slow, in the three layers with gamma ~0.5 in each and an optical density of ~0.70, was compared with several production run models of commercially available XR film (typically ASA 400, 10, 0.004, and an optical density ~3.60) using the output of a 3 mw helium-neon laser for imaging at a wavelength of 6328Å. Detailed images have also been recorded of an optically expanded beam including its diffraction patterns.

Detailed recording of these subjects has been accomplished utilizing the three sensitive layers of the various XR films and an evaluation of these images was made in order to determine the desired properties for future laser XR films. The major problem at the present time, in both Eastman Kodak and EG&G XR films, is the need for improved modular transfer function characteristics.

These improvements must come at the expense of film transparency. The transparency of these films is much greater than any XR film produced to date. One feature to the detriment of MTF is the absence of anti-halation layers.

Mono-layer XR films have been prepared by blending various emulsions and then coating them as a single layer. While the individual emulsions no longer retain their integrity in the blend (as shown, for example, by changing coupler and emulsion pairs), excellent XR-type film properties have been gained. Various experiments were performed with development rates, image transfer, and emulsions which produces the XR properties in a blended emulsion. The present contention is that significantly different reaction rates or equilibria between developer oxidation products and color couplers are functioning, and that one dye may be formed to the exclusion of another until the concentration of oxidation products reaches values where a second dye may begin to form.

Another model consisted of several layers of the same silver halide emulsion with the effective speed being modified by interlayers of soluble black dyes. This, of course, is quite similar to the use of reflective mirror interlayers, also proposed in the program. However, black dyes, which although offering a technically simpler approach, result in energy absorption which lowers the energy tolerance of the film. The "mirror" approach would not absorb energy, but rather direct it away from the film.

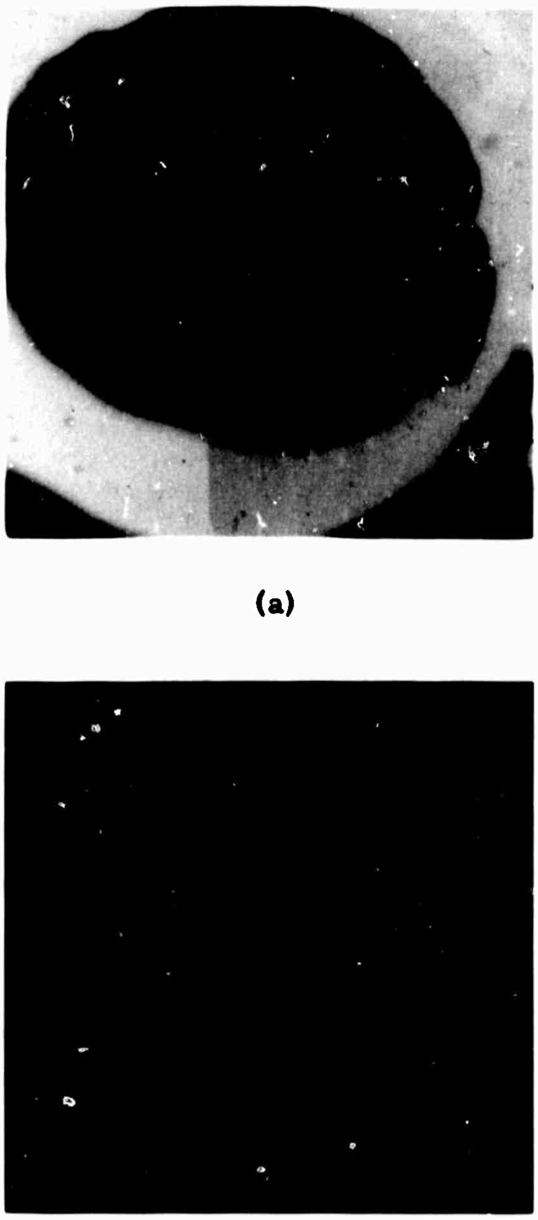
The use of soluble black dyes (model LXR-5) as attenuators and the improvement of modulation transfer function characteristics have not been pursued beyond initial evaluation, which indicated them to have broad windows in their absorbance.

Vapor-deposited silver mirrors (thickness 50 Å, d = 1.25) on acetate base have been obtained from Hy-sil Corp., Revere, Massachusetts. Silver halide emulsions have been found to adhere well to this morror surface and also to permit the mirror coating to be lifted from its base and become part of the emulsion. Exposures of the mirror-gelatin composite to a one joule/$cm^2$ ruby laser have resulted in destruction, and silver coatings will probably not be sufficient. The technique of incorporating silver mirrors into the film structure was quite satisfactory. However, some material other than silver (such as a dielectric) is required for reflecting the energy.

Another film was designed to record the emission of a Korad Model K1Q ruby laser, pulsed at one joule/$cm^2$. The first tests to establish design criteria consisted of exposing neutral density filters to the laser pulse. It was determined that an optical density of less than 0. 10 was required to prevent plasma formation and destruction of the filter. This has also been borne out in practice with films. However, there have been some notable exceptions. The relationship of material damage, photolysis and plasma generation to the physical and chemical properties of the film such as turbidity or silver concentration is only imperfectly understood and must be the subject of some detailed examination.

Clear triacetate film base and gelatin are found to be transparent and unaffected by a one joule/$cm^2$ ruby laser pulse. Slow Lippmann compositions ($d = 0.05$) have also been found which are undamaged by this laser. Kodak fine grain positive film which has less sensitivity at 6934 Å, exhibits extensive photolysis, gelatin charring, and saturation upon development. However, the same emulsions with and without color couplers or different dyes with similarly sensitizing characteristics did not give photolysis or film damage in every case. Results obtained by exposing film in a vacuum or in air have led to the contention that plasma formation might occur in some emulsions and generate ultraviolet radiation which would expose the film.

Typical examples of film saturation and film damage produced by high energy lasers are shown in Figure 15. Both the images on Kodak fine grain positive and Modified XR were obtained using the maximum beam filtration (ND 0. 1) possible without filter damage.



(a)

(b)

Figure 15. Typical images of 1 joule/cm$^2$ ruby laser emission recorded on conventional films (a) Kodak type fine grain positive (b) Modified XR.

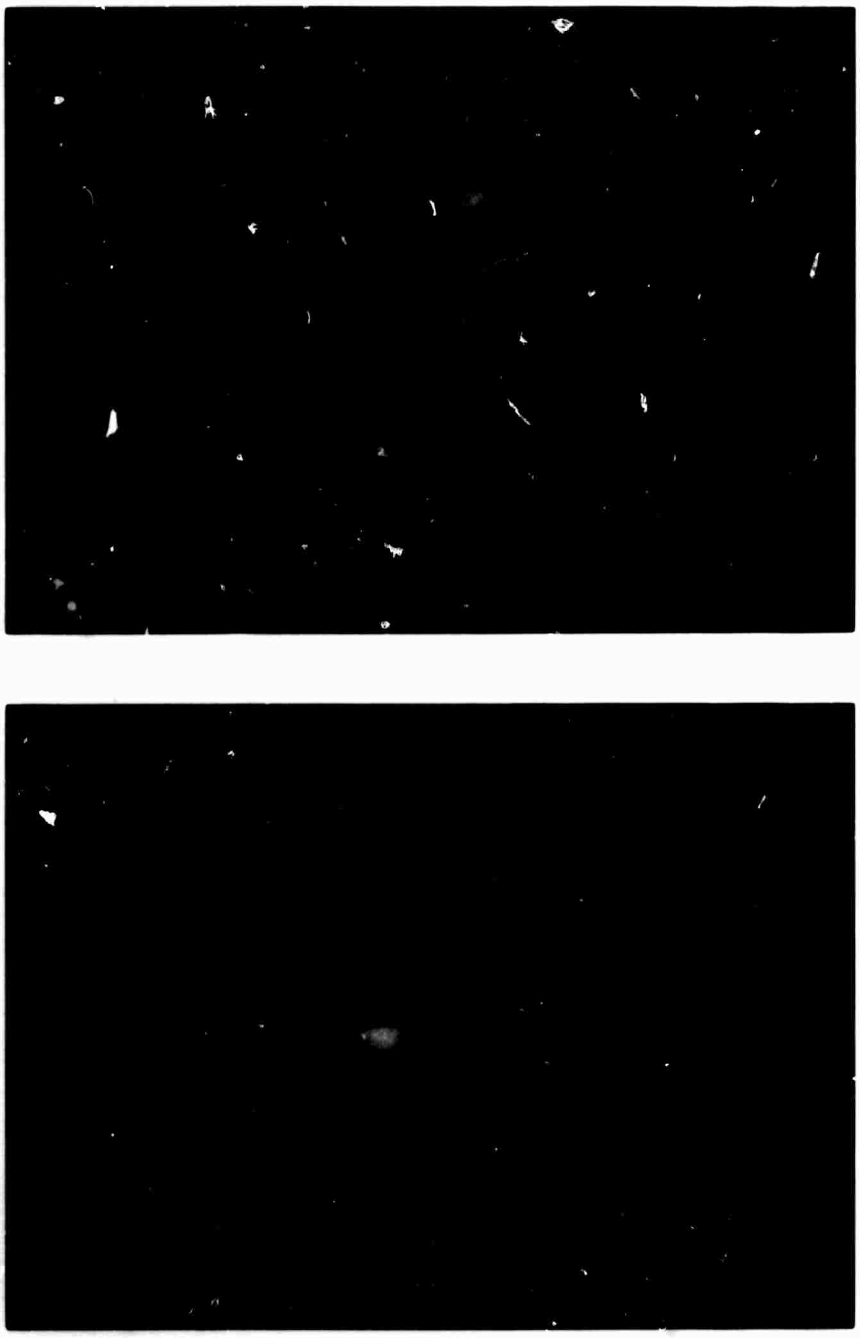


Figure 16. Images of 3 joule/cm$^2$ ruby laser emission recorded on LXR-10 film.

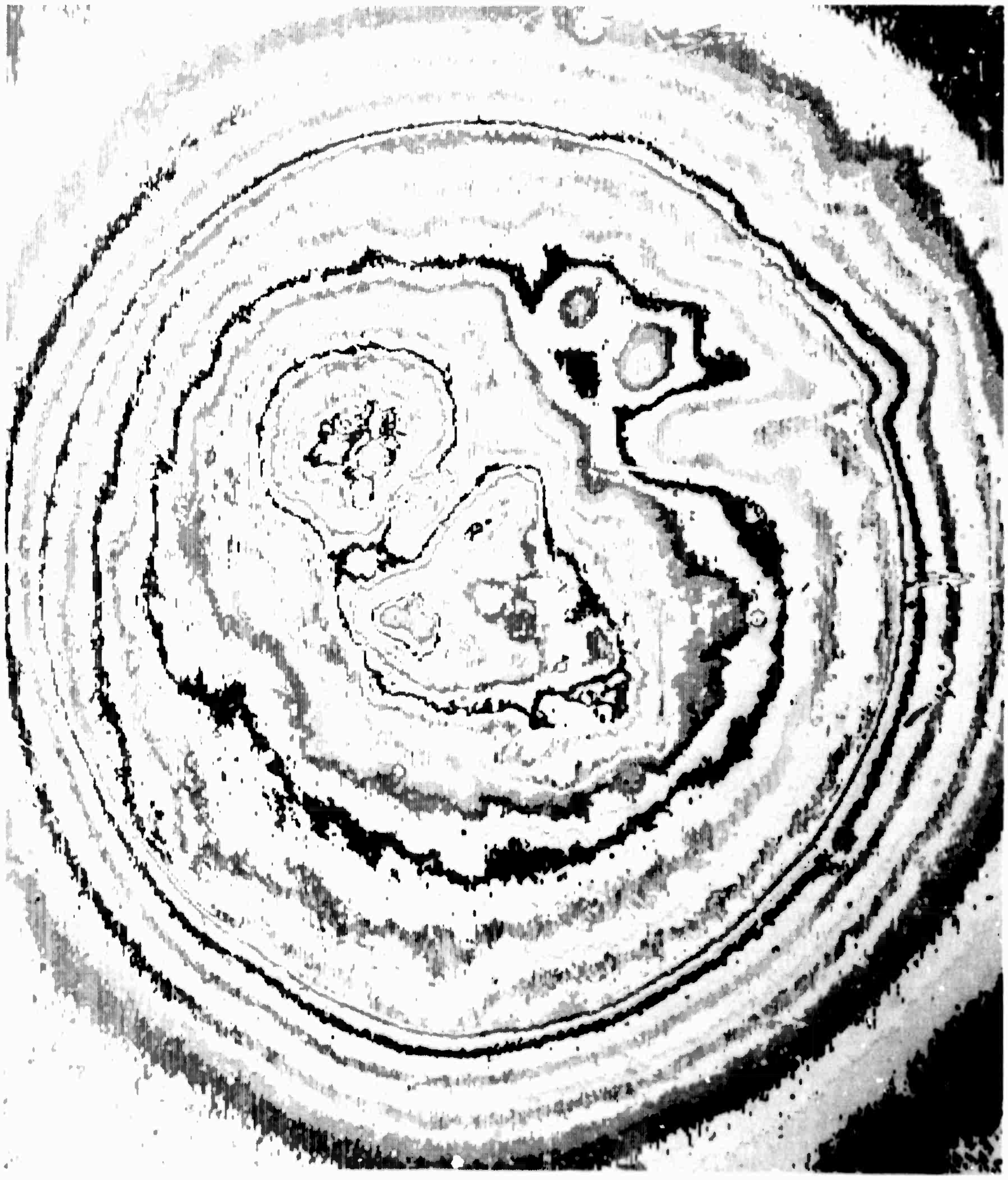


Figure 17. Isodensity recording of upper image in Figure 16.

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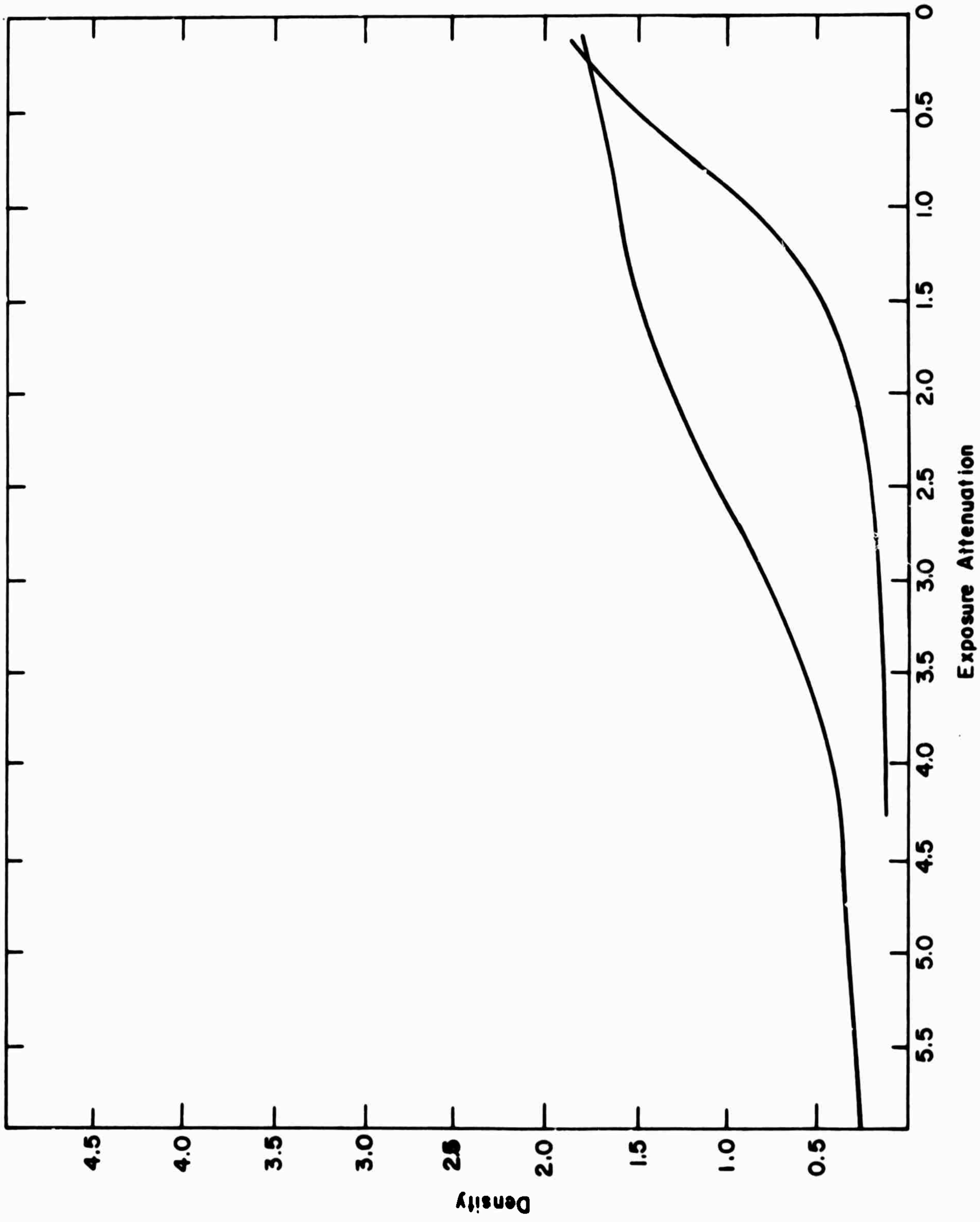

Figure 18. Characteristic curves of LXR-1O.

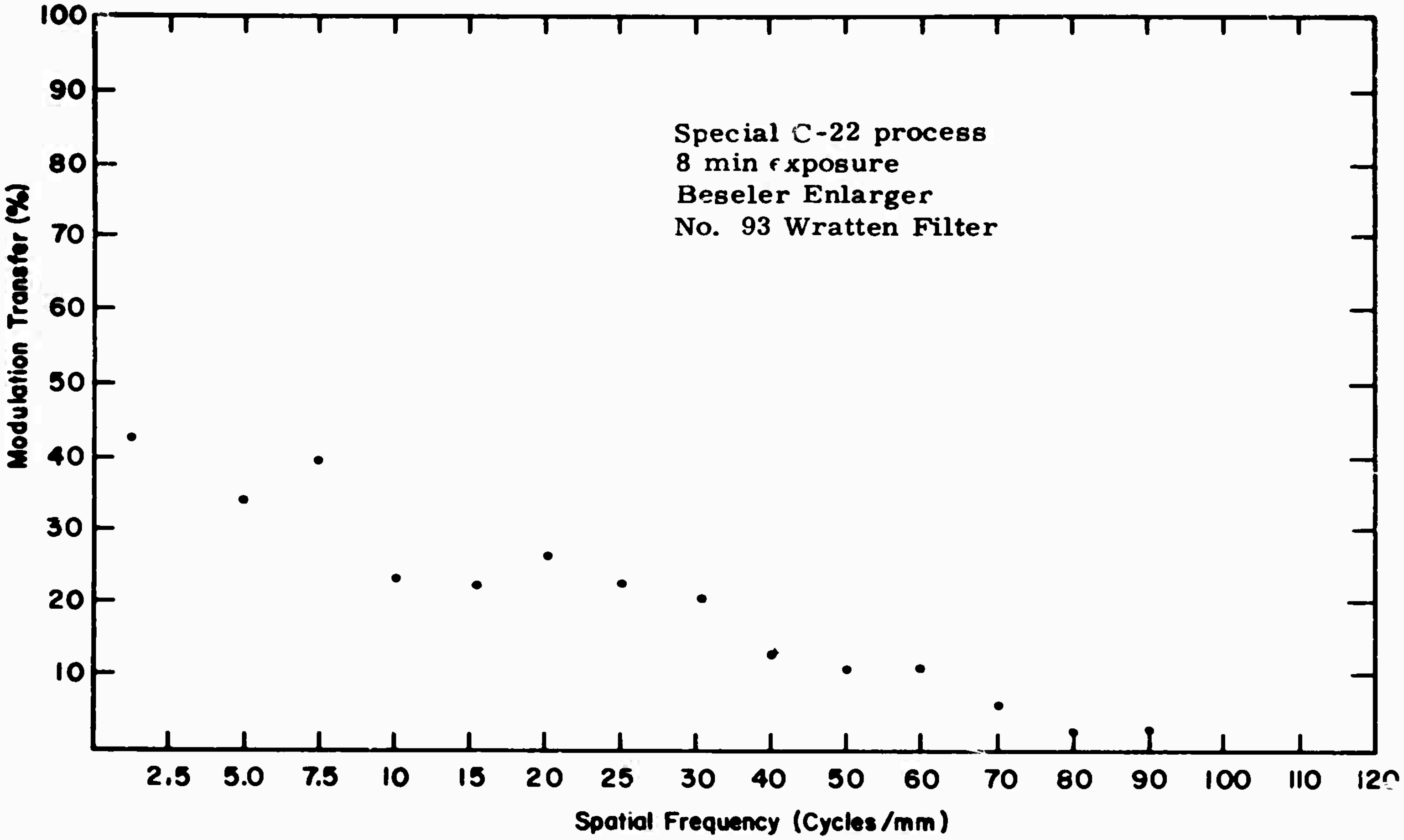

Figure 19. MTF characteristics of magenta layer of LRX-10 film.

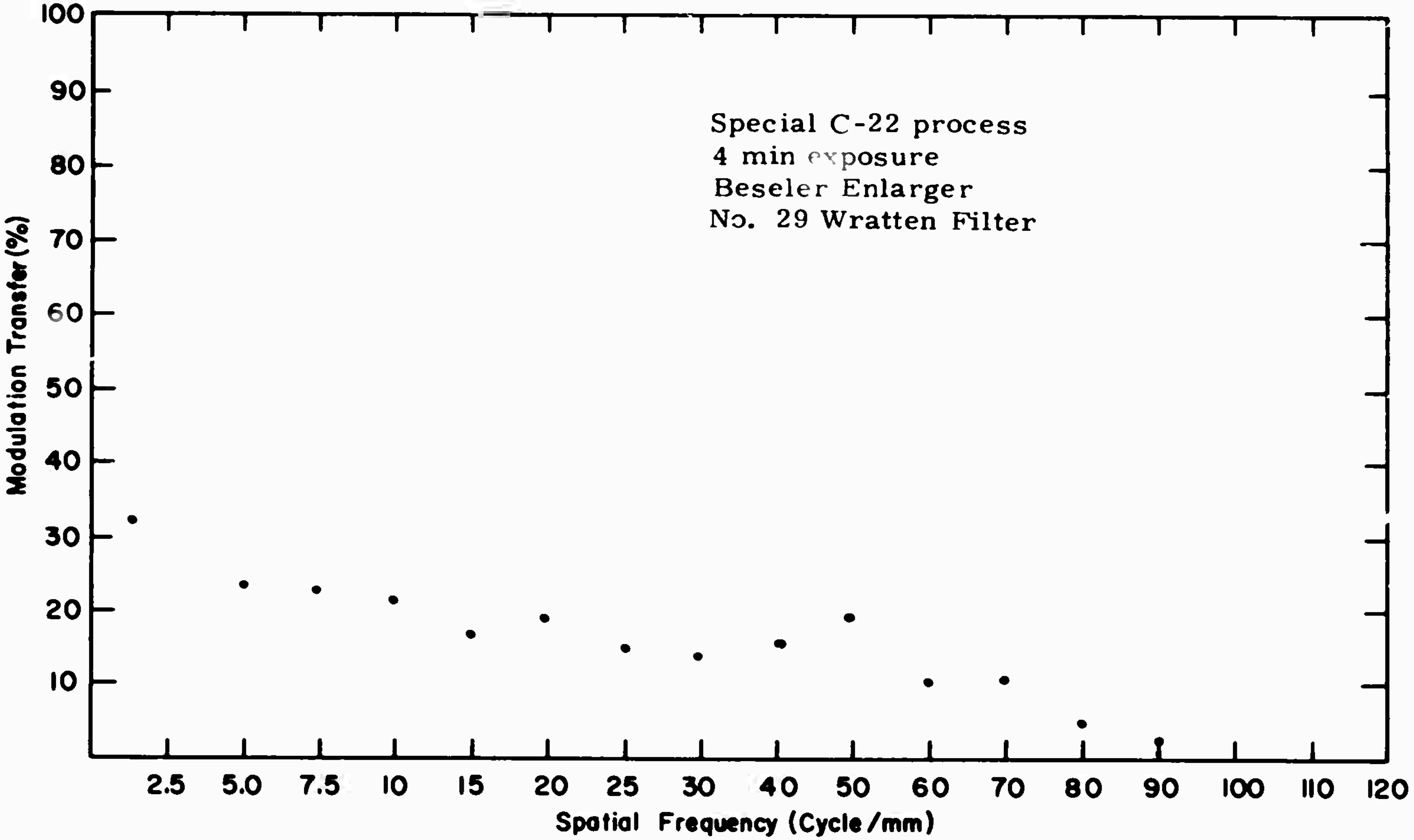

Figure 20. MTF characteristics of cyan layer of LXR-10 film.

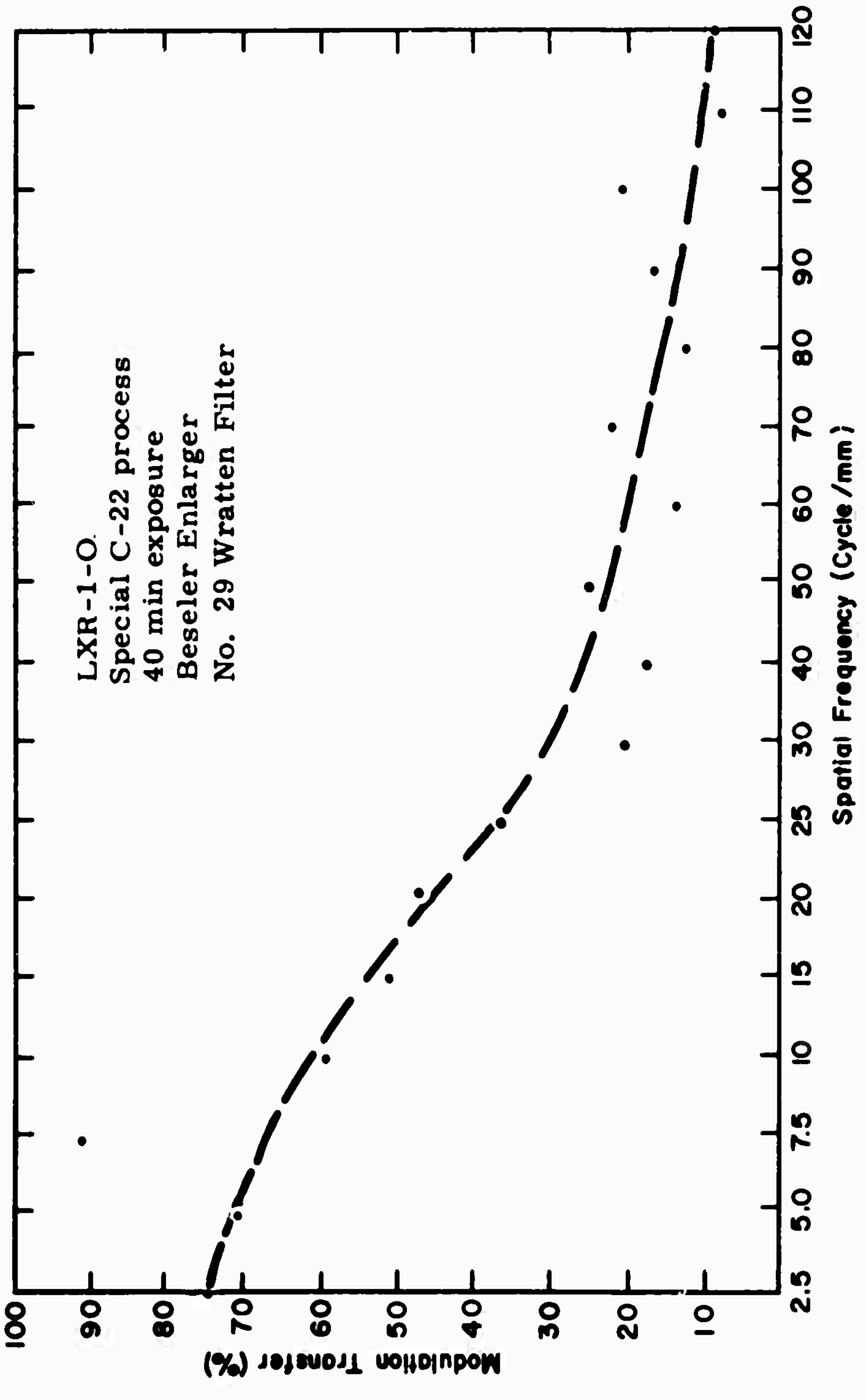

Figure 21. MTF characteristics of cyan layer of LXR-1O film.

The apparent resolution was determined to be 181 l/mm for the magenta layer, 288 l/mm for the cyan layer and 141 l/mm for the layers in combination. Accutance was determined at density 1. 52 and was 150 D/mm$^2$ for the magenta layer and 121. 5 D/mm$^2$ for the cyan layer. The low apparent values in resolution and acutance are caused by the unique photographic characteristics of LXR-1 film such as transparency, low sensitivity, and long toe region and are discussed in greater detail in Section 4.

LXR-2 Films

The third objective of the program, the development of LXR-2 photochromic photographic materials, was also realized. The concept of providing photographic images of lasers by the reversal of the colored state of a photochromic molecule was first successfully demonstrated using commercially available photochromic materials coated on a polyester film base. American Cyanamid photochromic film type 43-540, 43-540A and 51-142 were found to give a repeatable exposure density relation for fixed levels of ultraviolet pre-exposure and temperature. The pre-exposure was of 60 second duration using a 150 watt MacBeth xenon arc about 15 centimeters from the film. This exposure is not critical providing that saturation (density ~1. 0) is achieved. Exposure to the lasers followed immediately to avoid background degradation.

Exposure to the emission of a 3 mw/cm$^2$ Spectra Physics Model 122 helium-neon laser resulted in images in a minute or less (exposure energy value ≤ 0. 2 joules/cm$^2$) which were stable up to several hours depending upon ambient temperature and lighting conditions. Preliminary exposure density curves were determined using a uniformly irradiated spot obtained by reflecting the laser beam from a diffuse surface and directing the energy through a small, fixed aperture varying the intensity with filters. The energy passing through the aperture was computed from the manufacturer's specifications. A mechanical shutter was used to control the exposure, and the resulting image transmission for the various exposures was measured on a microdensitometer. It became evident that the photographic sensitivities of the three systems were comparable although their optical absorption character varied significantly. Preliminary tests over an exposure range of 1.0 to 100 sec. at 1.0 to 3.0 mw/cm$^2$ indicates severe reciprocity failure. The materials are much more sensitive to high intensity illumination for short exposures than lower intensity for longer exposure times. The rather high contrast characteristics of this film make it a sensitive means for measuring small variations in laser beam intensity. Although the absolute sensitivity of the film is rather low, it is quite adequate for high power laser beam recording situations. The resolution capabilities of the film (>250 l/mm) in its usual application suggest that very fine details of laser beam patterns can be accurately recorded.

Undoubtedly, other types of photochromic films will produce different photographic characteristics. During this phase of the program, the objective was to develop materials with preselected sensitivity, broad exposure latitude, improved exposure reciprocity and to investigate photochromic image stabilization. Triarylmethane leucocyanides and spiropyrans were selected for investigation since the literature described them in greatest detail. The stability of the colored state of these photochromics can be modified several orders of magnitude by the discrete choice of substituents on the aromatic rings as well as by the concentration of cyanide or other anion with the triarylmethanes. To this end, very pure samples of malachite green leucocyanide (λ max in ethanol 633 mμ versus 632.8 mμ for helium-neon laser emission) and 6'-nitro-1, 3, 3-trimethylindolinobenzopyrylospirans (6'-nitro BIPS), 6'-nitro-8'-methoxy BIPS and 6-nitro-5'-7'-dichloro BIPS and some others were prepared by literature techniques. (Appendix D). The rate constants for decolorization vary from 10$^{-6}$ to 10$^{-2}$ in the BIPS compounds.

Film coating and casting techniques were also subjected to extended study. While this appears relatively straightforward, it is necessary to consider polymer, photochromic, plasticizer and activators in some detail to obtain clear high resolution and photosensitive materials. The photochromic compounds have only slight sensitivity as crystals. Because of this, solvents such as hydroxy compounds, polyethers, phosphoric esters, and primary and secondary amines are added to the films as activators. A typical emulsion is made by dissolving a methacrylate polymer, the photochromic and $\beta$-(-p-tert-butyl-phenoxy) ethyl alcohol in toluene, which when dried at the proper rate gives a usable material.

Methods of stabilizing the photochromic image to prevent the indiscriminate bleaching of the film due to the so-called dark reaction were also found in the literature. A particularly effective method for the spiropyrans consists of exposing to a HCl vapor atmosphere for 2 to 5 minutes. This converted the colored spiropyran to an unidentified yellow compound which fades within a few days. A strong, reversed image is then formed by exposing the stabilized films to ultraviolet light, the stabilized areas remaining essentially colorless with the original background becoming colored. Immersion in a steric acid bath is effective in preventing the conversion of the triarylmethane dyestuff into the leucocyanide.

A number of materials have been tested to determine their response to the emission of a carbon dioxide laser made available to us by NASA Electronics Research Center, Cambridge, Massachusetts. The particular laser used produced a 2 x 6 mm beam at 0. 25 to 3. 0 watts. This laser was not particulary useful for recording beam characteristics since it was operated using an AC-powered discharge tube. However, it was useful for determining energy response values for the materials tested.

From the results of these tests, it is evident that there are many materials which are affected by the $CO_2$ laser emission (10.6μ), including the 3M thermofax system, American Cyanamid and EG&G photochromics, Corning photochromic glass and various thermographic papers. In general, images became perceptible with the laser operating at 0.25 watts with one second exposures, except for the case of the photochromic glass which was less-sensitive by an order of magnitude. H&D curves and more quantitative evaluations will be generated upon completion of the $CO_2$ laser under construction at EG&G. None of the photochromics were sensitive to ruby laser emission.

The first objective, the production of modified XR film, was accomplished. The film possesses previously unrealized photographic speeds and extended red response as well as marked improvements in grain structure and exposure reciprocity.

Extensive experiments with emulsion formulations, and dye, coupler, hardener, reflector, and coating technologies have also resulted in advanced silver halide laser recording films. Techniques for preparing silver halide emulsions with minimal opacity have been developed. Oil dispersion and non-diffusion coupler technology have resulted in color Lippmann emulsions (apparent ASA $10^{-2}$ to $10^{-8}$), possibly for the first time. Color forming emulsions with speeds as high as ASA 400 have also been developed. Appropriate development procedures for each emulsion type have been devised. Synthesis of infrared sensitizing dyes has been accomplished and silver halide emulsions have been sensitized to beyond one micron. Techniques for continuously coating 35 mm film in uniform structurally sound 500 foot lengths of film, containing as many as fourteen layers have been developed. Various film models have been prepared and evaluated sensitometrically. Factors critical to laser recording have been identified, and films capable of recording the emission of a 45 joule/cm$^2$ ruby laser have been made. These films are capable of recording directly in the beam without being damaged.

The concept of providing photographic images by reversal of the colored state of photochromic systems has been successfully demonstrated using a helium-neon (0. 633$\mu$) and carbon dioxide (10. 6$\mu$) laser. The photographic and thermal factors influencing image stability were investigated and chemical methods of stabilizing photochromic images have been developed.

In addition, several other important photographic achievements were made such as emulsions with high sensitivity times resolution figures of merit, emulsions with six orders of magnitude exposure latitude, monolayer XR films and emulsions with IR sensitivity in excess of primitive sensitivity.

Several literature reviews relating to state-of-the-art laser recording and potential non-silver systems were conducted.

Further experimentation and analysis will lead to improved recording media for use in high energy laser diagnostics and holography. The following areas for additional investigation are presently apparent.

Silver Halide Emulsion Research. Despite the considerable progress which has been made by applying the methods of physics and chemistry to the scientific control of the different steps of emulsion formulation, the preparation of the photographic emulsion is still largely empirical, and will remain so as long as the causes of sensitivity and the exact nature of the photographic latent image are not known. While the results of emulsion formulation is an art belonging to the practice rather than to the theory of photography, the requirement of precise control also reflects the availability of a broad latitude of photographic properties. Silver halide emulsion research remains the principal area for the advancement of photography, and therefore the major emphasis of the program should continue to be placed upon it.

During the program, a wide variety of emulsions were prepared to achieve the objective of producing a satisfactory medium for the recording of high energy laser emissions. The design of a film capable of recording the high energy levels of present laser systems, yet having useful exposure latitude, contrast, and response in the ultraviolet, the visible, and the infrared region requires the most advanced emulsion technology for optimization of a number of competing effects. General experimentation should continue in the areas of complex interactions of materials, emulsification, digestion, washing, and sensitization in emulsion development as they relate to the present requirements for the highest degree of transparency, for low sensitivity, for wide latitude and normal contrast in ultrafine silver halide grains, and for maximum utilization of developed silver to produce desired densities in the thinnest coated layers.

In addition, the following specific investigations are initially required:

1. Experimentation with high iodide content Lippmann emulsions to determine causes of very high sensitivity increases with retention of transparency to the green and red. Investigation of inorganic and organic additives for tailoring gamma. Investigation of developer formulations to cut time of processing.

2. Experimentation with high bromide content ASA 40 Lippmanns with the objective of retaining the sensitivity while improving the gamma.

3. Experimentation with silver-gelatin-coupler ratios to minimize the amount of gelatin required to diminish hardening interaction with the CIBA couplers while still affording sufficient protection to insure ultrafine silver halide grain size.

4. Investigation of $10^6$ latitude emulsions through low temperature precipitation of Lippmann emulsions.

5. Investigation of thiosulfate, gold, and gelatin sensitization of transparent high speed emulsions. Investigation of the causes of fog and low gamma in chemical sensitization.

6. Investigation of the adaptability of zirconyl sulfate emulsion precipitation to high gelatin content Lippmann emulsions for improvement of transparency and sensitivity through washing.

7. Investigation of the factors influencing stabilization of emulsion sensitometric properties, particularly hardening aging and coupler-gelatin interaction. Investigation of film image aging.

8. Investigation of the minimization of by-products in the synthesis of infrared sensitizing dyes to increase dye absorption on silver halide grains.

9. Investigation of extension of silver halide spectral sensitivity to far infrared with colloidal silver or gold.

10. Investigation of the strong infrared sensitization in high dye concentration fine grain emulsions.

11. Investigation of the balancing of processing in different emulsions in multilayer film through iodide content and organic developing accelerators and inhibitors.

12. Investigation of the incorporation of couplers during processing to increase transparency and eliminate coupler-emulsion interactions.

13. Investigation of monolayer XR film containing emulsion blends and the kinetics of color development.

14. Investigation of the application of Land's photo-solubilization by incipient development for producing sensitivity gain in Lippmann emulsions having the minimum fine grain silver content.

Non-Silver-Halide Recording Media. Non-silver halide light sensitive systems are the subject of considerable research and development as a natural consequence of the growing influence of silver halide photography. Although some of these non-silver halide systems have been known for more than a century, information about them has, until the publication of a recent monograph by Kosar,[11] been confined to scattered journal and patent citations. The volume of publication is accelerating annually.

The low photographic speed, spectral sensitivity, and high resolution offered by non-silver halide photographic systems make them potentially attractive for laser emission recording applications.

In our consideration to continue the investigation of photochromic systems as infrared recording media, a number of related systems were examined, for example:

Hershel Effect - A silver halide emulsion which has been exposed to blue light and subsequently exposed to infrared before it is developed is found to undergo a reduction in the effect of the original exposure.

Thermodiazo - Thermal development of diazotype images.

Dye Bleach - Formation of photographic images by the bleaching of dyes.

Photothermographic - Development of photographic latent images by subsequent application of heat.

Kalvar - Thermal formation of microscopic gas vesicles in a plastic medium arising from photodecomposition of nitrogen compounds.

As in the photochromic systems, infrared images are produced in the Hershel effect, photothermographic, and Kalvar systems after prior uniform exposure to an ultraviolet source.

The principal disadvantage of any thermally active system is the lateral conduction of heat from the image area during exposure, since this results in a considerable loss of resolution. A quantitative estimate of this effect should be performed in each case.

An infrared photographic system based on the Hershel effect should produce high quality images of the infrared. If the films that are devised in this program can be effectively sensitized with colloidal silver, reversal processes and present commercial products based on them would offer no advantage. The other systems form directly viewable images (after ultraviolet pre-exposure) which is an advantage in laser development research. The photothermographic systems have not been worked out well and offer the further disadvantage that the images are generally of metallic mercury and therefore unstable. Thermodiazo systems have a disadvantage in that the maximum obtainable image density is limited by the speed with which the recording matrix can be heated. The Kalvar process exhibits a narrow exposure latitude, while the time and temperature acheived during exposure have a marked effect on the characteristic curve. The images are generally viewed by projection. Gamma may be advantageously varied, however, by changes in the viewing illumination. The images are also self-filtering and once formed, are less susceptible to damage owing to the dispersing characteristics of the image when exposed to additional laser emission. The dye bleach systems, of which the photochromics are a special case, are truly photographic rather than thermal acting (photochromics in many cases excepted). These systems also exhibit acceptable gammas, may be spectrally selective or have broad spectral response depending on the choice of dye, give high resolution, and exhibit no exposure reciprocity failure. The high initial optical density of both dye bleach and photochromic systems may suggest film destruction for the case of high intensity lasers. However, bleach-out images are advantageous for minimization of energy absorption by the recording medium. These systems also exhibit significantly broader exposure latitude than the others mentioned. The quantum yield is very low in dye bleaching, but approaches unity for the photochromics. Methods of stabilizing the images have been widely studied in both cases.

Overall, of these systems, the photochromics exhibit the best properties for laser recording, with distinct advantages lying in the other systems in specific instances.

Two other non-silver halide systems merit particular consideration. One system is based on liquid crystals and the other is based on free radical photography.

Liquid crystals are substances that physically resemble anisotropic liquids and have viscosities ranging from fluids to glass compositions. They optically exhibit many properties of crystals such as ability to scatter light in symmetrical patterns or to reflect different colors depending upon the angle of view. The liquid crystal phase of matter may be regarded as consisting of one- or two-dimensional crystals. Examples are found among cholesterol, benzoate, and anisole compounds.

The molecular structure of cholesteric liquid crystals can be rearranged easily. Thus, any small disturbance that interferes with the weak forces between the molecules can produce marked changes in such optical properties as reflection, transmission, birefringence, circular dichroism, optical activity and color.

The reaction of changes in color from minute changes in temperature is a most striking optical observation and the proposed basis for an infrared recording medium. Although most cholesteric substances are colorless as liquids, they pass through a broad and reproducible series of color transformations when cooled through their liquid crystal phase. By mixing cholesteric substances in various proportions, a wide variety of temperature-color combinations can be obtained. EG&G, Inc. recommends that the properties of liquid crystals as infrared laser recording surfaces be investigated. The investigation should include the formation of stable images by taking color photographs of the patterns produced in the liquid crystals by the temperature variations in the infrared laser beam.

Investigation of liquid crystal overcoats on color film is also recommended. In this system, a xenon flash, possibly with infrared removed by filtration, would be synchronized with the infrared laser pulse. The colored liquid crystals would then serve as filters in producing a stable color film image. Also the sensitometric properties and image quality of the systems should be assessed.

The second system, reaction with arylamines of free radicals generated from organic polyhalogen compounds by radiation has been utilized as a negative working print-out process by Sprague, Fichter and Wainer.[12.] A broad range of sensitivities and spectral response was observed with ASA speeds from 0. 1 to zero reported. The most suitable amines are claimed to be secondary arylamines in the presence of N-vinyl amines, while the halogenated compounds used in the process are usually prehalogenated alkyl derivatives. By suitable choice of the organic halogen compound, the spectral sensitivity can be properly controlled so that it is possible to adjust the sensitivity to the energy available from a given light source.

Addition of leuco bases of triphenylmethane dyes in certain of the systems increases the sensitivity, contrast, spectral response and post exposure red light intensification. Sensitivity to 7000Å and greater has been reported. Styryl dye bases are also effective amines. They are available in wide varieties and can be selected so as to give a full range of sensitivities to visible light. Since the systems are also temperature-sensitive, infrared laser sensitivity seems assured. It is the panchromatic response of these systems which is the principal basis for our recommendation for consideration for additional research.

A literature review has also been conducted in an attempt to recommend a representative list of systems for evaluation as potential components of other model films within the following categories of non-silver halide systems: (1) Inorganic Systems; (2) Dichromated Colloids; (3) Photopolymerization Processes; (4) Diazo Processes; (5) Dye Formation and Bleaching; and (6) Thermography.

An attempt was made to select systems composed of readily obtained materials while retaining the representative character of the recommendations for the various broad classes of non-silver halide recording processes. Some laboratory examination should be made to determine what advantages may exist. The literature will be continuously assessed for new systems. Representative systems are given in the following list:

A. Inorganic Systems

1. Cuprous chloride (Z. Physic Chem. 202, 403 (1953)).
2. Copper acetate and ascorbic acid (Acta Chem. Scand. 15, 888 (1961)).

3. Copper salts and easily oxidized and reduced ions, e.g. Cobalt hydroquinone (Roczniki Chem. 34, 999 (1960)).

4. Copper sulfate and anthroquinone sulfuric acid or sodium hydrosulfite (US 2504593).

5. Yellow mercuric oxide with sodium iodide and sodium thiosulfate.

6. Mercurous tartrate, citrate, oxalate (US 2732304, US2459130, US 1939232, US 2095839, US 2933389).

7. Thallium salts (Phot. J. 86B, 100 (1946); Sci. Ind. Phot. 17, 193 (1946); Phot. Korr. 93, 67 (1957); US 1880503).

8. Phospho and silico molybdic and tungstic acids (J. Opt. Soc. Amer. 44, 699 (1954)).

9. Ferric chloride, ferric ammonimum oxalate, potassium ferricyanide and other ferric salts (US 1213925; Sci. Ind. Phot. 22, 125 (1951) J. A. C. S. 84, 4027 (1962), US 2398986, US 2137015, US 2130071).

### B. Dichromated Colloids

1. Colloids with organic dyes (Z. Wiss. Photo. 25, 394 (1928); US 1, 984090; Zh. Naucki i. Prikl Foto. 8, 303 (1963); Atelier Phot. 37, 98 (1930).

2. Colloids with inorganic ions (J. A. C. S. 81, 5543 (1959) and US 3074794).

### C. Photopolymerization Processes

1. Ethylenic compound-benzoin-polyethylene glycol-dimethacrylate (US 2, 760, 863).

2. Cellulose acetate hydrogen phthalate, triethylene glycol diacrylate, N, N'-methylene-bis-acrylamide, anthraquinone, p-methoxyphenol and mucochloric acid (Br. 883, 558).
3. Cross linkable polyamides (Br. 795, 961).
4. Peroxides polymerization of methacrylamide (Trans. Faraday Soc. 59, 1369, (1963)).
5. Vinyl monomers and ferric ammonimum oxalate (US 3, 136, 638).
6. Vinyl monomers and titanium dioxide and zinc oxide (US 3, 041, 172, US 3, 147, 119).
7. α, α'-azobisisobutyronitrile (J. A. C. S. 71, 2661 (1949).
8. Photo reducible dyes (Z. Wiss. Photo. Z6, 171 (1928); Z. Phys. Chem. B15, 18 (1931); Proc. Roy. Soc. A189, 481 (1947); J. Polymer. Sci. 7, 243 (1951); US 2, 734, 027; J. A. C. S. 79, 4836 (1957). J. A. C. S. 74, 5808 (1952).

D. Diazo Processes

1. General diazo (US 2, 322, 982; Chem. Ind. 22, 146 (1944); Inter. Blue Print 35, 15 (1962).
2. Metal-diazonium processes (J. SMPTE 54, 345 (1950)).
3. Vesicular process (J. SMPTE 73, 213 (1964); US 2, 703, 756).

E. Additional Processes involving Photochemical Formation and Sistruction of Dyes

1. Photochemical Formation
    a. Arylsulfonyl compounds of aminonapthol sulfonic acid (US 2416021).

b. Condensation of amines and aldehydes or ketones (US 2426894).

c. Diazo sulfones (US 2465760).

d. Polymer degradation of vinyl and vinylidene compounds. (Phot. Eng. 4, 133 (1953), US 2, 772, 159).

2. Photochemical Bleaching

1. Thioxanthonium and selenoxanthonium dyes (US 1850220, US 1880573, US 2097119).

2. Oxonium dyes (US 1880573).

3. Xanthoxolium dyes (US 2097119).

F. Thermography

1. Heat sensitive recording papers (US 1880449, US 1897843, US 2336299, US 2681277, US 2732299, US 2813042, US 2855266, US 2929736, US 2625494).

2. Thermographic Copy Papers.

a. Calcium, magnesium and zinc stearate (Br. 922, 999).

b. Titanium dioxide in polymers (US 2916395).

c. Methylene blue and mercuric stearate (US 2880110).

d. Thermofax paper.

e. Heavy metal soaps and couplers (US 2663655, US 2663656, US 2663657, US 2663658).

f. Dyes in waxes (Br. 894, 527, Br. 941, 827, US 2939009).

g. Ektafax paper.

2. Cellulose acetate hydrogen phthalate, triethylene glycol diacrylate, N, N'-methylene-bis-acrylamide, anthraquinone, p-methoxyphenol and mucochloric acid (Br. 883, 558).

3. Cross linkable polyamides (Br. 795, 961).

4. Peroxides polymerization of methacrylamide (Trans. Faraday Soc. 59, 1369, (1963)).

5. Vinyl monomers and ferric ammonimum oxalate (US 3, 136, 638).

6. Vinyl monomers and titanium dioxide and zinc oxide (US 3, 041, 172, US 3, 147, 119).

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   c. Methylene blue and mercuric stearate (US 2880110).

   d. Thermofax paper.

   e. Heavy metal soaps and couplers (US 2663655, US 2663656, US 2663657, US 2663658).

   f. Dyes in waxes (Br. 894, 527, Br. 941,827, US 2939009).

   g. Ektafax paper.

h. Polyethylene and dye (Ger. 1166795).

i. Indoles and phenol (US 2967785).

j. Diazoamino dyes with naphthol couplers (US 2995465).

k. Rubednic acid and nickel salts (US 3111423).

l. Triphenylmethane dye carbinol and chloroacetamide (US 2940866).

m. Substituted benzothiazole and dichloroethyleneamines (US 3129109).

Laser Sensitometry and Image Evaluation. Sensitometry is concerned with the relationships between the silver (or other) deposits or impressions formed in a photographic image and the factors of exposure and processing to which the photographic media have been subjected. Since the onset of photographic science, emphasis has been placed on the methods and limitations of experimentation and instrumentation for sensitometry and image evaluation for the calibration of films. It is unfortunate that the developments in sensitometry have not kept pace with the laser research and development that has taken place during the past eight years. The problems involved in evaluating the response of photosensitive media are complex when the radiation has the unique properties of coherence, high photon flux, monochromaticity, and the short exposure times frequently found in laser emissions. Though simulated or indirect methods employing conventional radiators are more convenient to use, they are subject to failures and misleading results because they cannot conform to laser properties. A laser as a source of radiation is truly unique so lasers must be used if the evaluations of the film are to be realistic. One of the more important differences between a laser and a source of simulated emission can be given by way of example. All films have some form of interface with a medium which has a different index of refraction. In the case of an emulsion, or emulsions, coated on a film base, there are two interfaces, the interface between the emulsion and the base, and that between the emulsion and air. The interface between the emulsion and the air does not have any effect, as energy which is reflected does not enter into the film and is not recorded.

Because of the physics of light, there is a critical angle beyond which energy hitting the film base will be reflected by the film base back into the emulsion. In conventional photography anti-halation backings absorb some of the energy so that it will not be reflected into the emulsion. This reflected energy becomes part of the sensitometry of the system since the amount of light reflected is generally about the same under most conditions. In laser direct beam recording, where the degree of coherency is much higher than normally obtained in other conditions, this internal reflection is much less since less of the energy is likely to hit at the critical angle. Thus, there is a marked effect on the sensitometric results which will not be approximated by conventional light sources. The use of a laser should be considered carefully, as it has many problems which make some sort of simulation very desirable. Laser emission is inherently non-uniform in cross-section, since it contains diffraction patterns and general regions of high and low intensity. Sensitometry requires a uniform and reproducible source. Reducing the laser emission to a pure gaussian distribution can be accomplished by spatial filtering, and very careful alignment of the laser optical components. This reduces the energy considerably, however, and makes it difficult to evaluate slower materials. For faster films, this technique must be used. For films which are designed for high energy lasers, this technique may not be applicable even when the beam is focused down. It will then be necessary to work with the beam as it is emitted from the laser. This technique is rather crude but for some materials may be the only way to get this type of data.

The film evaluations of specific interest may be conveniently classified as energy toleration, sensitometric characteristics, resolution, and image evaluation.

Energy toleration is the simplest measurement as it requires only methods of providing accurate assessment of energy per unit area at several levels to the point of destruction of the photographic material. The most direct approach is to evaluate the material response by subjecting it to a laser beam focused to different diameters. In a focused beam the energy levels required to damage film produce ionization in air. This results in spurious energy and different wavelengths and forms a shield which absorbs energy. The evaluations should be performed in vacuum to obtain absolute destruction levels.

The sensitometric and spectral sensitivity characteristics of a film are very difficult to obtain accurately. If a film has been designed to record only a specific laser, its response to a broad range of wavelengths may be of only minor interest in view of the experimental difficulties encountered in determining its spectral response. The conventional method is that of using a wedge spectrograph, in which a direct graphical presentation of the spectral sensitivity of a material to a particular source is gained by using a diffraction grating to disperse the source onto a neutral grey wedge require long exposure times. Since laser films are very insensitive and suffer from unusual spectral reciprocity failures, exposures greater than $10^{-6}$ seconds are misleading or entirely useless.

Special techniques are also required to generate valid H&D curves. Normal methods will again be misleading because they do not allow for the narrow spectral energy distribution of lasers, the short exposure times of usual interest, or the specular qualities of the imaging material. Using conventional radiation to evaluate a laser recording medium requires a narrow spectral output unless the spectral response of the material is uniform throughout the region encompassed by the source. Exposure times must be as short as those used in the laser recording application unless an exposure reciprocity study has been performed. Such a study requires accurate operation of a laser over several orders of magnitude of time and intensity. Exposure-reciprocity effects are also wavelength dependent.

For high speed emulsions, it is possible to expand the laser emission over a circular grey scale to produce an exposure density sensitometric curve. The energy level of the emission must be below the destruction level of both the film and the grey scale. This level may be quite low in the high density regions of the scale.

In cases where the emulsion is too slow to allow the spread of energy over a grey scale, the beam must be accurately expanded to give a series of energy densities. This can be done either by using a number of expansion lenses or by using two lenses of sufficient diameter and varying the focal length. Ideally, the beam should be highly collimated. However, little error will be introduced under most circumstances if a diverging lens system is used instead of the beam expansion setup.

The study of the resolution of high resolution films is also very complex. They are often capable of recording much higher than normally can be utilized. There are many types of resolution which can be obtained when using these films, and care must be taken to utilize the form of resolution that has application for the recording subject and technique in question. The resolution obtained on a hologram for example, is grossly different from the resolution obtained when using direct beam recording.

Resolution obtained using direct beam recording must be present throughout the film if it is to be realized when the image is examined. Image resolution formed using holographic techniques has to be present only on the surface of the film. In fact, different images are recorded at different depths using holographic techniques. These two types of resolution can be very confusing, and can lead to some erroneous results. Each film may be said to have two or more resolution figures, which may or may not be the same.

Direct beam resolution is impossible to measure accurately unless a relatively complicated optical system is used. Resolution targets, or modulation transfer targets are of no use as they set up diffraction patterns when used with a highly coherent source. The simplest way to obtain a resolution target in this case is to use the Young experiment to obtain diffraction patterns of very high contrast and variable frequency whose values may be obtained by simple calculation. The processed film is then viewed with a microscope. This in theory would give 100% original modulation and the energy difference to the highest peak may be varied so that a valid modulation transfer scale is obtained. In a well adjusted laser, the modulation would be too great for any film, and some form of demodulation would be necessary. Calibration of the exposure range becomes a problem when trying to do this and is subject to large error. Peak and minimum energy for a large frequency can be obtained and exposure levels can be determined using a sensitometric curve that has been prepared using other means. This is making the assumption that the MTF at the large frequency chosen in 100%. If the same amount of modulation is used throughout the process, peak energy can be calculated, and the demodulation energy, usually a flash exposure, held the same. An MTF curve can then be obtained.

Surface resolution, which will be much higher than the resolution obtained for direct beam recording, is more useful for holographic work and gives an indication of the maximum resolution of the grains. The earliest technique to obtain this data was to make a Lippmann hologram of the spectrum and determine at what wavelength the film started to record.

A newer and more useful technique is through holographic reconstruction. This allows the determination of a resolution which is less than the wavelength of light. This resolution is higher than most emulsions are capable of recording even in depth.

To determine the limit of resolution, holograms are made in which the reference angle is varied. When the angle becomes too large, holographic reconstruction is impossible. This angle used in the following equation gives the limit of resolution.

$$D = \frac{\lambda}{2 \sin \frac{\theta}{2}}$$

| | |
|---|---|
| $\lambda$ | Wavelength of laser emission. |
| $\theta$ | Angle between reference beam and image beam. |
| D | Distance between lines recorded on film. |

This technique is very useful and gives valid data when the evaluation is for holographic work. Evaluation techniques for laser exposure require study and use of methods which are not used in evaluating films intended for conventional photography. Different methods of evaluating film are used depending on whether the film is to be used in direct beam recording or holography. Further, the use of a laser for the exposure is absolutely essential if the results are to be reliable, and care must be taken that the laser is used to yield results which are valid.

Holographic Films. The use of photographic film for holographic recording has placed additional demands on the properties of film and perfection of manufacture. In holography, the film is used in the aperture of an optical system rather than in the image plane. Geometric patterns are photographed and the record is placed in the optical aperture to control the phase of the transmitted light. This produces the desired effect in the image plane. Random variations in film thickness and refractive index affect the phase and prevent the desired results. Under these conditions any random variation in thickness, refractive index, or surface quality is of prime importance.

The two properties which make a photographic material suitable for holography are its photographic speed and resolution. Emulsions must be sensitized for the monochromatic radiation of the laser in order to record emissions in the visible and infrared. Since most panchromatic materials have already passed through their maximum sensitivity at the ruby (6943Å), helium-neon (6328Å) or neodymium glass (10600Å) wavelengths, special sensitizers must be used. The distance on a hologram between a line of highest density and one of lowest density corresponds to the difference in path length of half a wavelength between the reference beam and the object beam. For a helium-neon laser, if the angle between the reference and object beam is $45^{\circ}$ when incident on the photographic emulsion, this distance is $0.825\mu$ and can only be recorded by an emulsion having a resolution of 1250 lines/mm. In silver halide holography, the grain pattern of the emulsion is the basic noise carrier of image formation, and is also the holographic information carrier. The two-beam interference pattern may be regarded as a subcarrier modulating this grain pattern. Thus, an unwanted background of light scattered from grains is an unavoidable feature of silver halide holography which must be minimized. It is found then that the resolution of the reconstructed image is limited by the modulation transfer function of the film. The gamma of the film does not affect the contrast in the reconstructed image.

It is well known that high sensitivity and high resolution are contrary demands on the photographic emulsion. The light intensity available, the coherent duration of the wave front, the freedom from vibration of the object, and the demands on image quality will therefore be decisive to the suitability of a given photographic material.

The use of present continuous wave and pulsed lasers in holography, holographic recording media requirements, and evaluation of photographic film as an element of a coherent optical system has been the subject of many recent bibliographies and reviews (see Reference 13).

The high resolution,high speed films developed in this program should be considered as media for holographic recording as well as for laser calibration and diagnostics. While a detailed examination of such properties as modulation transfer function and noise spectrum as they manifest themselves in a coherent optical system is a major undertaking, the increasing requirements of holography suggest the consideration of the potential merits of the more promising films.

Application of High Speed Photography to Giant Laser Development. The recording of the spatial properties of the emission of a pulsed laser is usually time integrated. A method which would provide time resolution of these properties would yield a valuable description of the laser behavior.

The Electro-Optical Systems, Inc. Kerr Cell Framing Camera, Model KFC-600, is essentially a set of six individual 10 nanosecond Kerr cell shutters grouped around a common objective lens and a six-sided truncated prism, in which each face uses only its associated portion of the objective lens. A ground glass screen is used to obtain a ull pattern at each image plane of the six cameras grouped about the objective lens. Since all images are formed by the same lens system, each of the six cameras sees the laser emission from the same aspect. Associated with each of the Kerr cell shutter assemblies is a modular pulse generator with a pulse forming network. In order to examine the time dependence of a phenomenon, the six Kerr cells are pulsed in sequence. The six shutters are triggered independently through variable delays. The individual exposure times depend upon the pulse forming network associated with each Kerr cell, and the interframe times are adjusted from the control. System synchronization is obtained optically from the rotating prism. The optics and functioning of the Kerr cells and camera assemblies has recently been described.(14-16)

Dielectric Optical Filter. The transition between the amount of light reflected and the amount of light transmitted at the boundary surface between two transparent media is not abrupt. This was first studied in detail by Fresnel, and thus today this type of reflection bears his name. Depending upon the incident angle and the difference in the refractive index, light is reflected and transmitted in different amounts. Essentially, since none of the radiation is absorbed, this principle can and is being exploited with lasers without the material being destroyed in the process. The roof prisms and other reflecting prisms used with laser cavities are examples of Fresnel reflectors. Another example is the pellicle mirror, often used as a beam-splitter in the optical path of a giant pulsed laser beam.

An experiment performed in our laboratory suggests that an optical attenuating filter based upon the principle of Fresnel reflection might serve as an attenuator which could be incorporated within a photographic film. This would have the effect of permitting the film to tolerate a greater amount of energy before destruction. Such a filter would contain exceedingly small bubbles of air entrapped in a layer of gelatin. Gelatin, with a relatively high index of refraction relative to air, would cause the incident light to be reflected with only a small percentage being transmitted. The amount transmitted would be inversely proportional to the thickness of the layer. During processing of the film after exposure, the air bubbles contained in this layer would collapse resulting in complete transparency of a permanent nature.

A sample of such a filter was placed in the direct beam of a pulsed ruby laser and showed no evidence of change of state at an energy density level of one joule per square centimeter. However, the complete effects of such a filter upon image structure will require investigation in greater depth than the experiment permitted. It is believed that this will not present a serious obstacle.

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# APPENDIX A
# COMMERCIAL XR FILM DATA

**EG&G**
ELECTRONIC PRODUCTS DIVISION

EXTENDED RANGE FILM

DATA SHEET XR-18

**TECHNICAL DATA**

## EXTENDED RANGE FILM

A multilayer black and white negative film, for use over an extreme range of exposure. It is available in motion picture film, sheet film, in 35mm cartridges, and as aerial film.

### APPLICATIONS

XR Film is ideally suited for photography where the light conditions during exposure are unpredictable or where the subject exhibits a brightness range that varies over enormous limits. It has been used successfully in nuclear and non-nuclear explosions, rocket exhaust tests, laser photography, abortive missile launching evaluations and other similar applications.

### GENERAL DESCRIPTION

XR Film has three layers, all of which are panchromatically sensitized. The emulsion layers from top to bottom respectively are high speed, medium speed and low speed. Incorporated in the emulsion layers are dye forming couplers which react simultaneously during development to produce a separate negative dye image along with silver image in each layer. The dye images are yellow, magenta and cyan respectively. The silver images are removed later by bleaching, leaving only dye images.

Black and white positive prints are made from XR Negatives in a manner similar to that for making color separation positives from color negatives. Images in the top (fast) layer of XR are printed through a blue filter, those in the middle (medium speed) layer through a green filter and those in the bottom (slow) layer through a red filter.

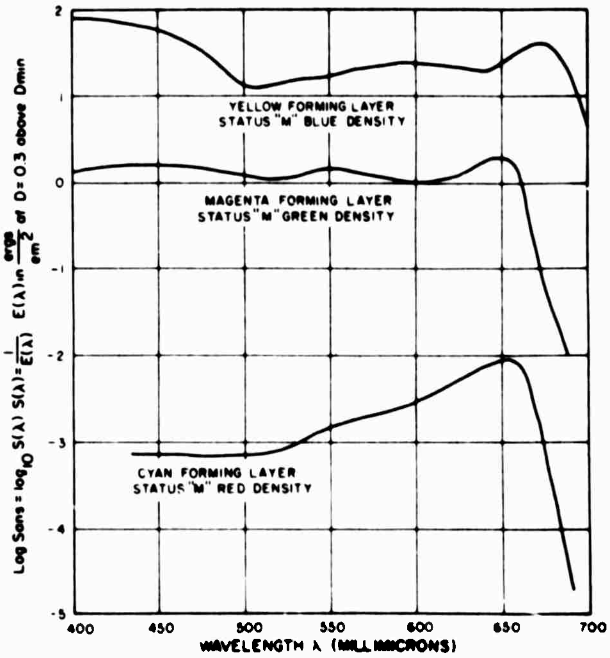
### EXPOSURE INDEX

| | |
|---|---|
| Fast Layer | 400 |
| Medium Speed Layer | 10 |
| Slow Layer | .004 |

These settings are recommended for meters marked for American Standard Exposure Indexes. It is virtually impossible to overexpose the slow layer in most applications. The user should take advantage of this characteristic and not risk underexposure. Note that XR is not an extremely fast film; if exposure conditions are so poor that only the fast layer is exposed, a more conventional film would do as well.

**COLOR SENSITIVITY:** Panchromatic

**SPECTRAL SENSITIVITY:** Sensitivity is the reciprocal of exposure (ergs/cm$^2$) required to produce a given density above the minimum value for each color image.



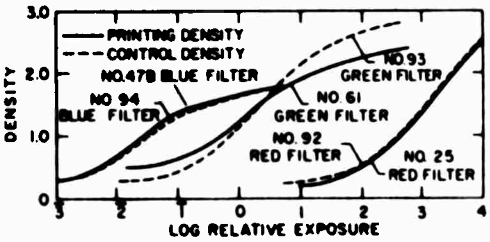
## RESOLUTION

| | |
|---|---|
| Fast Layer | 70 lines/mm |
| Medium Speed Layer | 50 lines/mm |
| Slow Layer | 30 lines/mm |

Exposure Time: 1.3 sec.
Densities are densities above base plus fog.

## D-LOG E CURVES

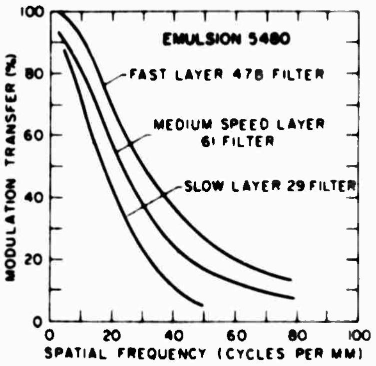
The curves show typical density vs. log exposure data from a $10^{-3}$ sec xenon flash exposure, and with normal C-22 processing. Densities as measured with a 3-color transmission densitometer are shown as dotted lines while printing densities through the recommended printing filters are shown as solid lines.



## MODULATION TRANSFER FUNCTION

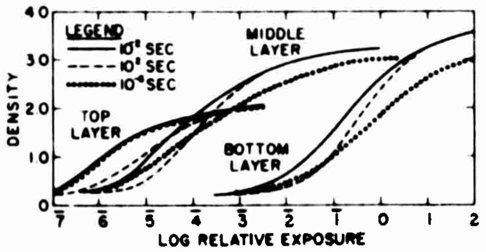
The modulation-transfer characteristics of a film indicate the effects that diffusion of light within the emulsion will have on the microstructure of the image. Image detail characteristics of a film used with an optical system may be predicted from the separate modulation-transfer functions for the film and the optical system.

The data is from a white-light exposure. The images were scanned with Wratten filter numbers 47B, 61 and 29 respectively for the fast, medium speed, and slow layers.



## RECIPROCITY FAILURE

Changes in speed or contrast or both occur with extremely short or extremely long exposure times. The curves show these changes for exposure times of $10^2$, $10^{-2}$, and $10^{-6}$ sec.



## SAFELIGHT HANDLING

Total darkness required.

## PROCESSING

XR Film may be processed by the user, commercial laboratories, or EG&G. For user processing, Kodak Color Processing Kit, Process C-22, contains all the chemicals for preparing a complete set of processing solutions. Developing time in the C-22 process is the same as that for Kodacolor; no special techniques are required.

Commercial color laboratories can process XR sheet film and short rolls of XR in their C-22 processing machines. Commercial motion picture laboratories offering Eastman Color Negative (ECN) processing can also process XR Film with no change from the normal ECN conditions. Such ECN processing is widely available for 35mm film. Service for 16mm and 70mm widths is not as widely available but can be obtained. Consult EG&G for current recommendations.

EG&G, Inc. offers processing, printing and analysis services for XR Film on a custom basis. For information contact EG&G with your specific requirements.

## DUPLICATE NEGATIVES

Standard color film duplicating procedures can be followed. 16mm color reversal duplicates from 16mm or 35mm XR motion picture film are available through most motion picture laboratories.

## EXAMINATION OF NEGATIVES

Filters must be used to view XR negatives in normal contrast. In white light with no filter the yellow image is almost invisible; with a blue filter, the yellow image (fast layer) is visible with good contrast. Similarly, the magenta image (medium speed layer) is seen through a green filter, and the cyan image through a red filter.

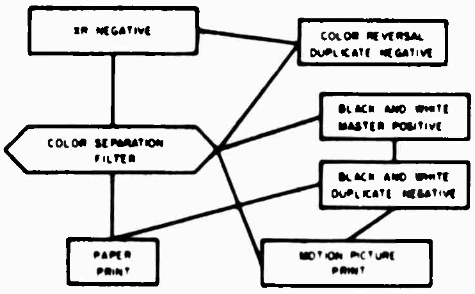
## PRINTING

### PRINTING FLOW CHOICES

The diagram illustrates the present printing possibilities. First, a duplicate XR negative can be made on a color reversal duplicating film; an example would be a Kodachrome duplicate. The original or duplicate XR negative can then be printed through a color separation filter, resulting in a paper print or motion picture print. Where one or very few prints are needed, the direct method of printing is usually used. The master positive/duplicate negative method would be used if a number of prints requiring elaborate local printing of a subject were needed. The local printing corrections would be necessary only once—in making master positive. The other use of the master positive/duplicate negative technique would be for motion picture printing. The black and white duplicate negative could be intercut with conventional negative footage and printed on a normal blue-sensitive release positive film.

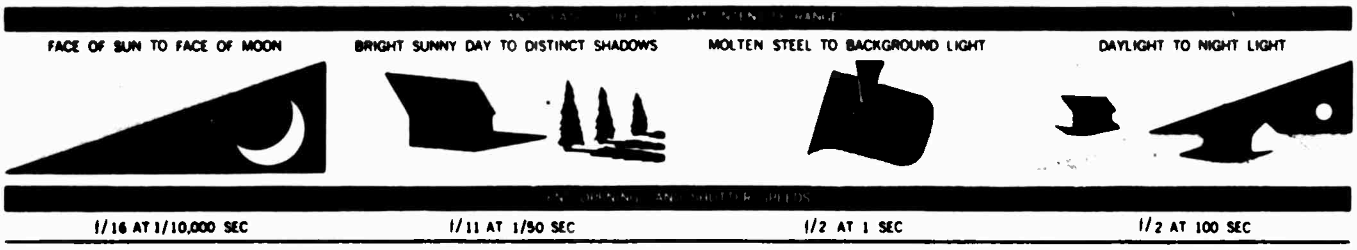
Materials to be used for direct filtered prints must be panchromatically sensitized if all three filters are to be used. Kodak Panalure and Ansco Panadex papers are designed for making black and white prints from color negatives and are suitable for XR printing. Obtaining motion picture printing materials for 16mm is difficult, but suitable print films are available for 35mm. Eastman Pan Separation Film Type 5235 can be used for direct prints, master positives, and duplicate negatives, but can be obtained only in 35mm. Eastman Fine Grain Panchromatic Duplicate Negative Types 5234 or 7234 would also be satisfactory for use as a master positive in either 35mm or 16mm sizes when used with Eastman Fine Grain Duplicating Positive Types 5365 or 7365 as a duplicate negative.

For 16mm direct separation printing, two products are suitable. Both are panchromatic microfilm negative films and are available in 16mm perforated only on special order. One is Recordak type 7459 AHU Film from Eastman Kodak Company, Business Systems Market Division and the other is Remington Rand Microfilm Type 1K, from Remington Rand Systems, Division of Sperry Rand Corporation. Both of these films should be developed in a low energy, negative developer (D76) for a short time to reach the desired gamma of about 2.0.



### PRINTING FILTERS

The filters used to make prints from XR negatives are the same types as those used to make color separations from color films, since the dyes in XR film are very similar to those in color film. Satisfactory Kodak Wratten Filters are Blue Nos. 47 or 47B, Green No. 61, and Red No. 25. The choice of filter for XR is not very critical—other similar color



EXPOSURE GUIDE TABLE

separation filters will do nearly as well.

Due to differences in the emulsion layers of XR film, the layers vary in certain characteristics which should be considered when making black-and - white prints.

1. The (fast) yellow layer of XR film has a coarser emulsion grain pattern than the (slow) cyan layer, which has a fine emulsion grain pattern. Therefore, in making prints, the user should anticipate that the grain pattern will vary from layer to layer and that prints made from an XR film negative that is predominantly yellow will be more grainy than prints made from an XR film negative that is predominantly reddish-purple.

2. A broad range of composite black-and-white prints, showing detail from two or more layers in a single frame, can be made by conventional dodging techniques using the appropriate color filters.

## STORAGE

XR Extended Range Film gradually loses speed and contrast as it ages. These changes occur more rapidly at high temperatures (above 75°F) than at lower temperatures. To extend the useful life of the film by retarding these changes, it is recommended that the user refrigerate XR film at 40°F or lower. Film to be used within 30 to 60 days from receipt of shipment need not be refrigerated unless storage temperatures are expected to exceed 75°F. If the film is to be kept for a longer period or ambient storage temperatures are likely to be above 75°F, the unopened packages of XR film should be stored in refrigerator or freezing unit. When the packages of film are removed from cold storage, they should be allowed to stand unopened until they have reached approximate room temperature to avoid condensation of moisture on the film surfaces. Approximate warm-up times are as follows: For roll film, a 25°F rise in temperature requires 1 hour for 16mm, 3 hours for 35mm, and about 8 hours for 5" aerial. (These times should be increased by about 50% for a 100°F rise in temperature.) For sheet film, a rise from cold-storage to room temperature requires about 2 hours for a 25-sheet package.

XR Film can be damaged by high relative humidities (over 60%). Therefore, packages of XR film should not be opened until the film is at room temperature and is about to be used. Further, open packages should not be stored in a refrigerator.

## NOTICE

"EG&G, Inc. warrants XR film to be free from defects in manufacture, labeling, and packaging and that all such film returned to it for processing will be handled in accordance with the highest industry standards. EG&G's liability under this warranty shall be limited to replacing with an equal quantity of unexposed film any XR film which is returned to EG&G and found by it to be so defective or which is lost or damaged by EG&G. The buyer is expressly notified and agrees that all implied warranties, including specifically those of merchantability and fitness for a particular purpose, are excluded and that EG&G shall in no way be responsible for consequential damages whether or not due to negligence of EG&G. Dyes used in the film are subject to change with time and, accordingly, the film is not warranted against change in color."

For further information, contact: XR Customer Service Department.

*All Data and Specifications Subject to Change Without Notice*

## APPENDIX B
## STANDARD SILVER HALIDE EMULSIONS

During the emulsion formulation phase of this program, a large number of emulsions were investigated to determine the effect of synthetic parameters on their photographic properties. The following formulas were used as the basis for the preparation of particular emulsions.

### MODIFIED BASIC LIPPMANN EMULSION

| | | |
|---|---|---|
| I. | Gelatin | 8.0g |
| | Distilled Water | 75.0cc |
| | Silver Nitrate | 2.0g |
| II. | Gelatin | 8.0g |
| | Distilled Water | 75.0g |
| | Potassium Bromide | 1.4g |
| | Potassium Iodide | 0.02g |

The gelatin is soaked in the respective solutions for 1 hour at which time both solutions are warmed to the precipitating temperature (32 to 80°C). Solution A is then poured into solution B.

The emulsion is then chilled with cold water, noodled and washed for 1 1/2 hours.

The emulsion is melted and warmed to 35°C before use.

### EXTRA-RAPID AGFA NIGHT FILM FORMULATION

| | | |
|---|---|---|
| I. | Distilled Water | 70.0cc |
| | Potassium Bromide | 8.0g |
| | Potassium Iodide | 0.5g |
| | Gelatin | 1.0g |
| II. | Distilled Water | 90.0cc |
| | Silver Nitrate | 9.0g |

| | | |
|---|---|---|
| III. | Dry Gelatin | 25.0g |
| IV. | Distilled Water | 3.0g |
| | Potassium Thiocyanate | 0.03g |

Half of solution I is poured into solution II and stirred constantly at 70°C. The other half is added in 29 minutes. After waiting for one minute, the dry gelatin is added, and the stirring is continued for 20 minutes. Then the emulsion is cooled, noodled and washed for 1 hour.

The emulsion is then remelted, potassium thiocyanate solution added and digested until fog appears.

ATLANTIC GELATIN PRECIPITATED AMMONIA EMULSION

| | | | |
|---|---|---|---|
| I. | Gelatin | 6.0g | @40°C |
| | Potassium Bromide | 18.4g | |
| | Potassium Iodide | 0.4g | |
| | Distilled Water | 90.0cc | |
| II. | Silver Nitrate | 20.0g | @40°C |
| | Distilled Water | 60.0cc | |
| | Ammonium Hydroxide (29.0%) | q. s. | |
| III. | Gelatin | 23.5g | |
| | Distilled Water | 79.0cc | |
| IV. | Zirconyl Sulfate | 10% sol | |

V. Ammonium-Gold Thiocyanate: 6 cc. Gold Chloride ($HAuCl_4 \cdot 3H_2O$) 1% in 50 cc of 1% Ammonium Thiocyanate.

While stirring continuously, one half of solution II is added to solution I and digested for 45 minutes at 40°C. Then the remainder of II is poured into I. The emulsion is allowed to cool to 32-38°C, before the addition of 14 cc of concentrated hydrochloric acid and 2 cc of glacial acetic acid. The emulsion is then cooled to 32-38°C again and 30 cc of IV is added and stirred until a heavy, flocculent precipitate is obtained. The supernatent liquor is discarded and the precipitated emulsion is washed with fresh changes of 150 cc of cold distilled water twice within 5 minutes. Fresh changes of 150 cc of cold distilled water with vigorous stirring are then used every 5 minutes for a total of 45 minutes.

The precipitate is then soaked, with frequent vigorous stirring, for one hour in 120 cc of cold distilled water in which 0.4 g of a sodium bicarbonate has been previously dissolved.

The supernatant liquor is discarded and the precipitate soaked in 40 cc distilled water (room temperature) in which 2.0 g sodium citrate has been dissolved with vigorous stirring for at least 30 minutes.

With continuous stirring, the emulsion is then melted at 55°C and diluted to a volume of 210 cc. This emulsion is then added to III, the pH adjusted to 5.70 and 0.5 cc of solution V is added. A final digestion at 45-50°C is then performed.

## ATLANTIC GELATIN PRECIPITATED BOILING EMULSION

| | | | |
|---|---|---|---|
| I. | Gelatin | 9.0g | Prepare and hold at 70°C |
| | Potassium Bromide | 80.5g | |
| | Potassium Iodide | 5.0g | |
| | Distilled Water | 725.0cc | |
| II. | Silver Nitrate | 100.0g | Prepare and hold at 70°C |
| | Distilled Water up to | 800.0cc | |

III. Zirconyl Sulfate 10% solution

IV. Ammonium-Gold-Thiocyanate 6cc of 1.0% Gold Chloride solution ($HAuCl_4 \cdot 3H_2O$) in 50 cc 1.0% Ammonium Thiocyanate solution.

With continuous stirring throughout the entire precipitation process, 300 cc of solution II is added to solution I. Thirty seconds later the remaining 500 cc is added in 100 cc portions every 10 minutes. The completed emulsion is then digested for 20 minutes at 70°C.

The emulsion is cooled to 38°C and 40 cc of solution III is added to the stirring. The precipitate is allowed to settle for 5 minutes.

The supernatant liquor is discarded and the precipitate worked, with very vigorous stirring, with 700-800 cc of cold distilled water twice within 5 minutes. Then fresh changes of 700-800 cc cold distilled water, with vigorous stirring are made every 10 minutes for a total of 45 minutes.

The precipitate is next soaked with frequent, vigorous stirring in 700 cc distilled water in which 2g of sodium bicarbonate have been previously dissolved for one hour. The supernatant liquor is then discarded and the precipitate is soaked again with vigorous stirring in 100 cc distilled water in which 4.0g sodium citrate have been dissolved for at least 30 minutes.

## ATLANTIC GELATIN PRECIPITATED CADMIUM CHLOROBROMOIDIDE EMULSION

| | | E-22 | E-22b |
|---|---|---|---|
| I. | Distilled Water | 500.0cc | 500.0cc |
| | Gelatin | 15.0g | 15.0g |
| | Sodium Chloride | 12.0g | 0.0g |
| | Potassium Bromide | 10.0g | 10.0g |
| | Cadmium Chloride | 5.0g | 30.0g |
| | Citric Acid | 1.0g | 0.0g |
| | Potassium Iodide | 0.5g | 0.5g |

| | | | |
|---|---|---|---|
| II. | Silver Nitrate<br>Distilled Water | 38. 0g<br>400. 0cc | 38. 0g<br>400. 0cc |
| III. | Gelatin<br>Distilled Water | 25. 0g<br>100. 0cc | 25. 0g<br>100. 0cc |
| IV. | Gold Chloride ($HAuCl_4 \cdot 3H_2O$)<br>1% solution | 6. 0cc | 6. 0cc |
| | Ammonium Thiocyanate<br>1% solution | 50. 0cc | 50. 0cc |

The temperature of I and II is adjusted to 60°C and one half of II is added to I with constant stirring. After 10 minutes the remaining half of II is added. The emulsion is then digested for 45 minutes at 60°C.

After cooling to 30-40°, 75 cc of 10% zirconyl sulfate is stirred into the emulsion and the precipitate is allowed to settle for 5 minutes. The supernatent liquid is discarded and the precipitated emulsion is given two changes of 700-800 cc of cold distilled water with vigorous stirring within 5 minutes. The precipitate is then washed with further changes of 700-800 cc of cold distilled water every 10 minutes for a total of 45 minutes. The washed precipitate is then soaked with frequent stirring in 600 cc cold distilled water, in which 2g of sodium bicarborate has been dissolved. After one hour, the liquor is discarded and the precipitate further soaked with frequent stirring in 200 cc of distilled water containing 6g of sodium citrate for 30 minutes. The precipitate is then warmed to 55°C, one gram of citric acid and 0. 5g of cadmium chloride is added and the solution is diluted to 950 cc. 150 cc of the above emulsion is added to III and allowed to soak for at least 15 minutes, then digested at 60°C for one hour. 1. 0 cc of IV is then added and the emulsion is digested for an additional 5 minutes.

## CARROLL/HUBBARD FORMULA

| | | |
|---|---|---|
| I. | Distilled Water | 350. 0cc |
| | Ammonium Bromide | 42. 7g |
| | Potassium Iodide | 2. 3g |
| | Gelatin Iodide | 20. 0g |
| II. | Distilled Water | 450. 0cc |
| | Silver Nitrate | 60. 0g |
| III. | Dry Gelatin | 80. 0g |

Solution I is added to solution II in 5 minutes at a temperature of 70°C and allowed to ripen with stirring for 30 minutes. Solution III is then added. The emulsion is cooled then noodled and washed for 1 hour, at which time it is remelted and digested at 58°C.

## BAKER EXTREME SPEED EMULSION

| | | |
|---|---|---|
| I. | Potassium Bromide | 132. 0g |
| | Potassium Iodide | 4. 5g |
| | Gelatin | 50. 0g |
| | Distilled Water | 1000. 0cc |
| II. | Silver Nitrate | 150. 0g |
| | Water Distilled | 500. 0cc |

The gelatin is soaked for 1/2 hour, and brought up to 40°C when the components of I added.

Ammonia is added to solution II until the solution is again clear. Then solution II is added over a 5 3/4 minute period using a calibrated buret with moderate stirring.

The emulsion is allowed to ripen at 40°C for 40 minutes with stirring and then chilled rapidly. The emulsion is then stored under refrigeration for two days at which time it is noodled and then washed with running distilled water for 1 hour.

The washed emulsion is then melted and 140g of dry gelatin is added. The emulsion is finally digested to maximum speed.

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## SYNTHESIS OF 3, 3'-DIETHYL-9-11-NEOPENTYLENE-THIATETRACARBOCYANINE

The method of synthesis was adapted from the method of Haseltine(1) which consists of the condensation of the appropriately substituted benzothiazolium iodide in the presence of triethylamine and acetic anhydride. Detailed examinations of the preparation of several intermediates were made to obtain the dye precursors, and considerable experimentation was required to obtain the pure dye.

### Compound I - 3-ethyl-2-(1, 5, 5 trimethyl-3-cyclohexenylidine) methylbenzothiazolium iodide

(a) The first reaction in the preparation of this intermediate was the formation of a quaternary salt, 3-ethyl-2-methylbenzothiazolium-p-toluenesulfonate by reacting 2-methylbenzothiazole with ethyl-p-toluene-sulfonate.(2, 3) Equimolar quantities of the two reactants were heated together under reflux at 130°C for 24 hours. When cooled, the reaction mixture solidified to a hard, glassy, red material. Adding acetone to this and breaking up the solid left a white powder, which when filtered and dried resulted in an 83% yield of crude product (m. p. 151°C).

An attempt was made to purify this by dissolving it in methanol and subsequently precipitating it with acetone as prescribed in Glafkides.(3) However, we observed that the solid did not precipitate upon adding the acetone. As an alternative, the volume of the solution was reduced by allowing most of it to evaporate, and the precipitate was regained.

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(1) U. S. Patent 2, 756, 227.

(2) U. S. Patent 1, 846, 301.

(3) P. Glafkides, Photographic Chemistry, Fountain Press, London, 1958, V. 2, p. 769.

The material was pinkish in color. The pink color was removed by washing the solid with acetone. The melting point of this material was 162°-164°C, which is in good agreement with the value of 164°C cited in Glafkides.

(b) The second reaction in this preparation of compound I was the reaction between the quaternary salt described above and isophorone and the subsequent conversion to the iodide salt by treatment with sodium iodide solution.(4) One molecular part of the quaternary salt was heated with 2 molecular parts of isophorone under reflux for 16 hours at 135°C. After heating, the reaction mixture was poured into water and stirred. The aqueous solution was extracted 5 times with ether. The ether extract is very dark as is the aqueous solution. The reaction product is then precipitated by adding a solution of sodium iodide to the aqueous phase. The solution is chilled overnight to promote crystallization. The crude product was filtered and washed with water and dried. Yield of crude product was 50%. The crude product was recrystallized from ethanol and dried. The yield of product was 17% and the melting point was 231°C. The patent reference cites a product yield of 35% and melting point of 233°-234°C. Elemental analysis gave the following:

| Calculated | Experimental |
|---|---|
| 53.64%C | 54.4%C |
| 5.70%H | 5.7%H |

From the melting point correlation and the results of the elemental analysis, the synthesis of compound I has been considered effective in preparing the compound in sufficient purity.

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(4) U. S. Patent 2,756,227, Example 3.

Compound II - 2-(4-anilinobutadienyl)-3-ethylbenzothiazolium Iodide, exploratory experiments

(a) The first step in the preparation of this compound was the formation of the quaternary salt, 2-methylbenzothiazolium ethiodide. This was formed by reacting 2-methylbenzthiazole with an equimolar quantity of ethyl iodide.(5) The two reactants were heated under reflux for 20 hours at 110°C. After heating, the precipitate was filtered and washed with acetone. It was recrystallized from methanol. Upon drying, the material had a slight yellow color (m.p. 190°-194°C).

| Calculated | Found |
|---|---|
| 39.39C | 38.7C |
| 3.97H | 3.7H |

(b) The next reagent needed was β-anilinoacrolein anil or 1-anilino-3-aniloprop-1-ene. This was to react with the quaternary salt 2-methylbenzothiazolium ethiodide to produce compound II, 2-(4 anilinobutadienyl)-3-ethylbenzothiazolium iodide.

No direct reference to the procedure for carrying out this reaction was found. Glafkides(6) states that this reaction is carried out by warming the reactants as is done with diphenylformamidine which is similar in structure to the β-anilinoacrolein anil.

Therefore, it seemed reasonable that the procedure for the reactions of diphenylformamidine could be applied to those of the β-anilinoacrolein anil. A reference for the reaction of diphenylformamidine with a heterocyclic quaternary salt is found in British Patent 344,409.

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(5) P. Glafkides, Photographic Chemistry, Fountain Press, London, 1958, V. 2, p. 769.

(6) Ibid, p. 891.

The compound β-anilinoacrolein anil was not available commercially. No direct procedure for the preparation of β-anilinoacrolein anil was found either in Hamer(7) or Glafkides, although the latter states that this compound is obtained by heating propargylic aldehyde with aniline hydrochloride.(8)

The aniline hydrochloride was commercially available but the propargylic aldehyde (also called propargyl aldehyde, propiodic aldehyde, propynal) was not and had to be prepared in our laboratory. The compound propargylic alcohol was purchased as the starting material for this preparation. The usual procedure for the preparation of aldehydes from alcohols is simply to add an oxidizing agent to the alcohol. The oxidation is prevented from going all the way to the acid by distilling off the aldehyde as it is formed. This is accomplished due to the fact that the boiling point of the aldehydes are lower than the boiling point of the corresponding alcohol. In this oxidation of propargylic aldehyde, we were also concerned about the effect of the oxidizing agent on the carbon-carbon triple bond. Fieser and Fieser(9) indicates that the triple bond is sufficiently resistant to oxidation to not interfere with the oxidation of the alcohol to the aldehyde. During a preliminary attempt to perform this reaction by adding the alcohol to the oxidizing agent at the elevated temperature, the temperature in the reaction flask rose rapidly and an uncontrolled

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(7) F. M. Hamer, The Cyanine Dyes and Related Compounds, Interscience Publishers, New York, 1964.

(8) P. Glafkides: Op. Cit. p. 890.

(9) L. F. Fieser and M. Fieser, Introduction to Organic Chemistry, D. C. Heath & Co., Boston, Mass., p. 73.

reaction occurred. It was therefore deemed necessary to try and find a literature reference for this seemingly straightforward preparation. Several references to this preparation were found.$^{(10-15)}$

The procedure followed was that given in Reference 10, and was as follows: 400 grams of a 50% aqueous solution of propargylic alcohol in a distilling flask at 130°F was treated dropwise with 350 grams of potassium dichromate in 470 grams of $H_2SO_4$ in 1.1 kilograms of water. The distillate was then redistilled in vacuum with 1 gram of hydroquinone and gave 68 grams of propargylic aldehyde. In the preparation of this compound, the procedure as described in the literature reference was very carefully followed. Upon adding the oxidizing agent to the aqueous propargylic alcohol solution at 130°F, the dichromate solution became dark green. The solution was not boiling at this temperature and no distillate was being collected. With the external heat removed, the temperature of the reaction solution increased as more oxidizing agent was added until it began to boil at 97°C. Vapor temperature in the flask was 92°C and an oily liquid distillate began to collect in the receiving flask. The liquid

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(10) C. A. 47, 9997, (1953) Japanese Patent.

(11) Rabyah, Organic Synthesis Vol. IV, p. 813. Note in this reference--propiolaldehyde explodes on contact with alkali or rubber.

(12) C. A. 52, 10, 148f, German Patent 895, 897.

(13) Sauer, Organic Synthesis 36, 66-69.

(14) Wolff, Ber. 87, p. 668, 1954.

(15) Copenhaurer and Bigelow, Acetylene and Carbon Monoxide Chemistry, Rheinhold Publishing Company, New York, 1949, p. 124.

had a lachrymal odor and was a pale yellow color. The amount of distillate collected was approximately 55 grams.

No attempt to purify or redistill the product was made since it was felt that it would be easier to react it immediately with the aniline hydrochloride and purify that material. The propargylic aldehyde was also becoming a deeper yellow in color, indicating that some chemical reaction was taking place.

The procedure used in the preparation of the β-anilinoacrolein anil was to dissolve the 2 mole portions of aniline hydrochloride in water and add 1 mole portion of the propargylic aldehyde to this solution and heat under reflux for one hour. The addition of the propargylic aldehyde to this solution is accompanied by a considerable evolution of heat and it must be added slowly. As the aldehyde was added, the solution color changed from a pale green color to black and a reddish-orange precipitate began to form immediately. After one hour the reaction flask was removed from the heat, filtered and washed with water. The precipitate was a yellow-orange solid, that melted at 202°C

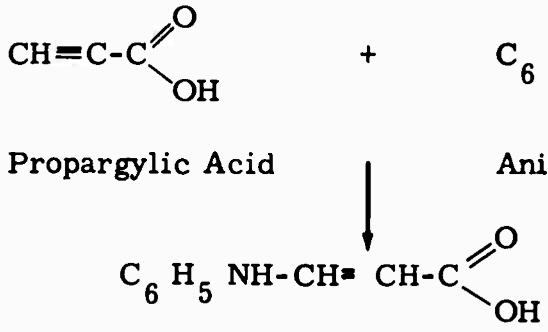
| Calculated for $C_{15}H_{14}N_2$ | Found |
|---|---|
| 81.03% C | 67.98% C |
| 6.36% H | 5.73% H |
| 12.60% N | 10.63% N |

Since the results of this analysis did not approximate the theoretical percentages, it was decided to repeat this step and attempt to recrystallize the product obtained from the reaction between the propargylic aldehyde and aniline hydrochloride. Additional propargylic aldehyde was prepared since the original had changed from a pale yellow to a dark orange-red liquid. The reaction was performed as previously described, and a portion of the aldehyde obtained immediately reacted with aniline hydrochloride. The orange-red precipitate was recrystallized from methanol and a light brown precipitate was obtained. The melting point of this solid was also 202°C. Since our yield was lower than expected, we attempted to make more by using some of the propargylic aldehyde made the previous day. The same procedure was followed except that this time the recrystallized product was a yellowish-orange solid with a melting point of 167°C. Analysis of these samples were as follows:

| Initial Product | 2nd Day Reaction | Theoretical |
|---|---|---|
| 67.05% C | 61.52% C | 81.03% C |
| 6.23% H | 6.60% H | 6.36% H |
| 10.50% N | 10.52% N | 12.60% N |

From the analysis it is obvious that the compound obtained was not the compound expected.

One speculation on the possible product leads to the following possible reaction. Assuming that the propargylic alcohol was oxidized all the way to propargylic acid, a possible reaction would be



$$CH{\equiv}C\text{-}COOH + C_6H_5NH_2HCl \longrightarrow C_6H_5NH\text{-}CH{=}CH\text{-}COOH$$

Assuming that this is the reaction product obtained, an elemental analysis of this compound would be:

% C = 67%

% H = 5%

% N = 9%

Experimentation and elemental analysis showed the product to be the anil hydrochloride rather than the anil. For $C_{15}H_{15}N_2Cl$:

| Theoretical | Found |
|---|---|
| 69.61% C | 67.98% C |
| 5.85% H | 5.73% H |
| 10.63% N | 10.83% N |

## Preparation of Compound II and the Neopentylene Dye

In the interim before it was realized that the hydrochloride salt of β-anilinoacrolein anil had been obtained, D. W. H. Hazeltine of Eastman Kodak was contacted to discuss the preparation. He suggested that instead of preparing β-anilinoacrolein anil by the reaction of propargylic aldehyde and aniline hydrochloride, that 1, 1, 3, 3 tetraethoxypropane may be reacted with aniline. The 1, 1, 3, 3 tetraethoxypropane is commercially available and this eliminates the necessity of preparing propargylic aldehyde. This procedure for making the β-anilinoacrolein anil hydrochloride is as follows:

> 0.2 moles (44g) of 1, 1, 3, 3 tetraethoxypropane and 0.4 moles (36g) of aniline are added to 125 ml of 3N HCl. The solution is stirred and heated to about 60°C for one hour. After a few minutes a reddish-brown precipitate begins to form. The precipitate is filtered and washed with a small amount of cold water. It is recrystallized 2 times from methanol to remove unreacted aniline. Yield of pure product is 35g or ~70%. M.P. is 212°-214°C. Elemental analysis calculated for $C_{15}H_{14}N_2Cl$ -- 69.61%C, 5.85%H and 10.83%N. Found 67.76%C, 5.91%H and 10.51%N.

To prepare compound II [2-(4-anilinobutadienyl)-3-ethylbenzothiazolium iodide] the literature(16) suggests heating the 2-methyl 3-ethylbenzothiazolium iodide and the β-anilinoacrolein anil to fusion. When the reactants were heated, the mix melted at 180°C. It was then heated to 200°C for 5 minutes. Upon cooling, a black ppt was obtained. Yield of product was 10% and melting point was 165°C. This was reacted with Intermediate I according to the procedure described in Example 13 of U. S. Patent 2, 756, 277. A small amount of product was obtained. The melting point was 194°C uncorrected. (Literature 198°C.)

The spectral sensitization test was performed by bathing Eastman Kodak fine grain positive film in a solution of the dye. The usual concentrations were 5 mg of dye in a liter of solution that was 75% water, and 25% methanol. The dye was first dissolved in the methanol which was then brought up to the proper volume by adding water. If 100 methanol was used the film curls excessively after drying.
The film was bathed in this water and methanol solution for 5 minutes and air dried. It was then exposed in the modified spectrograph and processed. Alternately, the dye was incorporated into emulsion E-13, using alcoholic solutions. When tested in the emulsion, the material sensitized the film at approximately 7000Å, but no infrared sensitivity was detected. Elemental analysis of the sample proved inconclusive as shown below:

| Theoretical | Analyst W | Analyst S |
|---|---|---|
| 60. 18% C | 51. 48% C | 58. 65% C |
| 5. 53% H | 5. 52% H | 5. 44% H |
| 4. 08% N | 4. 11% N | |

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(16) British Patent 344, 409.

An attempt was also made to prepare the dye by using the acetyl derivative of Intermediate II. This derivative was reacted with Intermediate I according to the procedure of Example 12 of U. S. Patent 2, 756, 277. The product obtained from this reaction was tested and found to sensitize a photographic emulsion to 7000Å. Intermediate II was also prepared by treating the acetyl derivation with conc. HCl.(16) The material obtained was reacted with Intermediate I as outlined in Example 13 of U. S. Patent 2, 276, 277. A small amount of precipitate was obtained, with melting point of 195°C uncorrected. It was tested to determine whether it sensitized a silver halide emulsion and it did to about 7000Å. From the data obtained, it appears that the dicarbocyanine dye was being prepared. This is reported in Mees and James to sensitize at 7000Å.(17) This results from 2 moles of the 2-methylbenzothiozolium ethiodide reacting with one mole of the β-anilinoacrolein anil.

Private communication with Hazeltine of Kodak confirmed that the dicarbocyanine was being formed. To minimize this reaction, the use of a mole excess of the β-anilinocrolein anil and also adding the solution to the quaternary salt to the solution of β-anilinoacrolein anil hydrochloride was explored. This solution was also made strongly basic by adding a large excess of triethylamine. This procedure is referenced briefly in Hamer in referring to the salts such as compound II. Even when the β-anilinoacrolein anil HCl was in 100% excess and with adding the quaternary salt solution slowly to the solution of the anil, some of the 3, 3'-diethylthiadicarbocyanine formed, as evidenced by photographic evaluation. The film exhibited a strong sensitivity peak at 6900Å. In

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(17) C. K. E. Mees and T. H. James, The Theory of the Photographic Process, MacMillan Co., New York, 1965, p. 202.

spite of this, this material was reacted with Intermediate I. The procedure was essentially the one described in Example 13 of U. S. Patent 2, 276, 277, except that 5 times the amount of triethylamine and acetic anhydride were used. The product obtained was tested to determine its spectral sensitization. The dye showed a strong sensitivity between 5300Å and 8000Å peaking at 6900Å (100 times the sensitivity at 4800Å) and continued sensitivity to a lesser extent out to 9500Å. It then appeared that the intended dye was sensitized along with the dicarbocyanine. It also appeared that it was necessary to use an amount of triethylamine greater than what is stated in the patent reference.

Spectral curves of a methanolic solution of the product which gave strong sensitivity at 7000Å and little or no sensitivity in the infrared showed an absorption peak at 850 mμ and another at 640 mμ. The peak at 640 mμ appeared when compound II is prepared by the reaction between 2-methylbenzothiazolium ethiodide and the β-anilinoacrolein anil hydrochloride. This is probably due to the dicarbocyanine when is formed by a by-product in the above reaction. Indeed, in a private communication with R. M. Sprague of Itek Corp., he stated that when these two materials are present in a strongly alkaline medium, the symetrical pentamethincyanine (dicarbocyanine) will always be formed. In this case we are probably only forming a very small amount since we are reacting these two materials on a mole to mole basis. To intentionally form the dicarbocyanine, normally one should use two moles of the quaternary salt to one mole of the anil.

When Intermediate II was prepared by a mole to mole addition and this product was used in the dye forming reaction, a methanolic solution of the dye showed an absorption peak at 640 mμ and 840 mμ. The peak at 640 mμ had a density of 2.00 whereas the peak at 840 mμ showed a density of 0.26. When Intermediate II was prepared by reacting one mole of the quaternary salt with two moles of the anil hydrochlories in a basic alcoholic solution, and then used in the dye forming reaction, the spectral absorbtion curve of the dye in methanol showed the same two peaks at 640 mμ and 840 mμ. In this case the densities of the peaks were 0.74 for 640 mμ and 0.77 for 840 mμ. The next logical step in this series was to further increase the mole ratio of anil hydrochloride to quaternary salt and also to add a solution of the quaternary salt to the anil slowly so that there was never an excess of quaternary salt. This should have minimized the possibility of a dicarbocyanine forming.

Another reference to the preparation of compound II was found in the literature.(18) The procedure is also referenced in Hamer(8) on page 214 and page 453. This material was prepared and used in conjunction with compound I to form the dye. There did not appear to be any reaction since the product which was filtered off physically resembled and had the same melting point as compound I. Sprague seemed to think that this procedure was incorrect and indicated that they had also tried it without any effective result.

It is also possible to prepare the dye via the acetyl derivative of compound II. This is to be preferred since it minimizes the chance of the dicarbocyanine forming. β-anilino anil hydrochloride was converted to the anil by treatment with a 10% sodium hydroxide solution. It was then added to an equimolar quantity of 2-methylbenzothiazolium ethiodide in acetic annydride. The product of this reaction was used in the procedure of Example 13 of Haseltine's patent. Dye solution after recrystallization showed only one peak of 840 mμ. The melting point of 199°C was in good agreement with Haseltine's 198°C.

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(18) F. M. Hamer, J. Chem. Soc., 35 (1949).

## PREPARATION OF 1:1'-DIETHYL-4:4'-CARBOCYANINE

5.98 grams of lepidine ethiodide in 400 cc of 95% ethyl alcohol was refluxed until all the air had been expelled by alcohol vapor. Then, a freshly prepared mixture of 20 cc in sodium ethoxide and 1 cc 4% formalin was added slowly during 20 minutes. Refluxing was then continued for 10 minutes and the stoppered flash was allowed to cool slowly. The solid which separates was dried in vacuum, washed with 80% alcohol, alcohol-ether and finally pure ether.

## PREPARATION OF 1:1'-DIETHYL-4:4'-TRICARBOCYANINE IODIDE

12 grams of lepidine ethiodide were dissolved in 25 grams of absolute ethyl alcohol and the solution chilled with stirring. This gave fine crystals of the quartinary salt. 5.6 grams of glutaconic aldehyde dianilide hydrochloride (from aniline and 2:4-dinitro-phenylpyridinium chloride) were added, the mixture stirred and 3.4 grams of piperidine added with cooling and stirring. A dark coloration rapidly developed and the solution was stored at 5°C for 24 hours. The dark liquors were filtered off and the crystals were washed with acetone and water. Next, the residue was boiled briefly with methanol, chilled and filtered.

3,3'-diethyl-9-methylthiocarbocyanine bromide and dicyanine A were used as received, from K. and K. Chemical Co. and Eastman Kodak Co. respectively.

The dyes produced spectral sensitivity in Atlantic Gelatin's precipitated boiling emulsion essentially as described in Mees and James.(17)

The photochromic compounds were prepared in accordance with procedures described in the general literature.

## TRIARYLMETHANE LENCOCYANIDES

These compounds were prepared after the method of Sporer(1) as follows (all syntheses were performed under yellow light that gave no wavelengths below 450 nm): The appropriate commercially available dye chloride or oxalate was dissolved in methanol and a concentrated aqueous solution of sodium cyanide was added while stirring at room temperature until the solution became almost colorless. Concentrated hydrochloric acid was then added until the solution attained a constant color. Sodium cyanide was again added to make the solution colorless. Hydrochloric acid was then added, and the procedure repeated until no color was formed. Water was then added to precipitate the leuconitrile which was then filtered and washed with water. To recrystallize the material, it was dissolved in a hot mixture of 500 ml methanol and 500 ml ethyl acetate. About 0. 1g of sodium cyanide was added to the solution. It was then filtered and refrigerated for a few days. The crystals were filtered and dried in vacuum at 50°C. The yields, melting points and analyses of the compounds prepared are given in the table below:

## BENZINDOLINOPYRYLOSPIROPYRANS

A mixture of equimolar amounts of the appropriate commercially available salicylaldehyde and 2-methylene-1, 3, 3-trimethylindoline in absolute alcohol was refluxed for 2 to 5 hours.(2) The resultant highly-colored mixture was cooled in an ice bath, filtered, washed with ethanol or an ethanol-water mixture and dried in vacuum at 50°C. The yields, melting points and analyses of the compounds prepared are given in the following table.

| compound | m. p. | analyses (%) calc. C | calc. H | found C | found H |
|---|---|---|---|---|---|
| New Fushine Leucocyanide | 256-<br>59 corr. | 77.49 | 6.79 | 77.16 | 7.00 |
| Malachite Green Leucocyanide | 188-89 | 81.09 | 7.04 | 80.85 | 6.85 |
| Pararosaniline Leucocyanide | 242-3 | 77.29 | 5.55 | 76.90 | 5.50 |
| 6'-NitroBIPS | 175.76 | 70.8 | 5.6 | 70.5 | 5.6 |
| 6'-Nitro-8'-methoxy-BIPS | 153 | 68.2 | 5.7 | 68.4 | 6.0 |
| 6'-Nitro-5', 7'-dichloro-BIPS | | 58.3 | 4.1 | 56.1 | 3.8 |

## REFERENCES

1. A.H. Sporer, Trans. Faraday Soc. 57, 983 (1961).
2. C.F. Koelach and W.R. Wockman, J.A.C.S. 74, 6288 (1952).

# APPENDIX E
# PREVIOUS AND RELATED CONTRACTS AND PUBLICATIONS OR ARTICLES

There have been no previous and related contracts or previously produced publications or articles resulting from total or partial sponsorship of the contract.

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# APPENDIX F
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**13. ABSTRACT**

Limitations of commercially available photographic materials for application in laser emission studies are described in terms of spectral response, sensitivity level, short dynamic exposure range and low tolerance to high energy densities. Commercially available XR film, which has a uniform response for visible light photography spanning nearly eight orders of magnitude, is not optimally suited for laser emission studies at > 6900Å nor does its high specular diffuse density allow the film to endure energies > 0.1 joule/cm$^2$. The results of studies with silver halide and photochromic emulsions and special XR film models specifically designed for use with laser emissions are summarized. The silver halide films not only have a $10^9$ dynamic range of exposure, but are responsive to a broader spectral range including wavelengths in the one micron region and have exhibited toleration to energy densities of 45 joules/cm$^2$. Further response to 10.6$\mu$ was found in photochromic films.

| 14. KEY WORDS | LINK A ROLE | LINK A WT | LINK B ROLE | LINK B WT | LINK C ROLE | LINK C WT |
|---|---|---|---|---|---|---|
| Laser Emission Recording | | | | | | |
| Wide Latitude Photographic Films | | | | | | |
| High Energy Tolerance Photographic Films | | | | | | |
| Lippmann Emulsions | | | | | | |
| Spectral Sensitization | | | | | | |
| Color Emulsions | | | | | | |
| Laser Emission Sensitometry | | | | | | |
| Photochromic Compounds | | | | | | |

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