Device Photolithography:

Thin Photosensitive Materials

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New camera systems, utilizing lenses of high numerical aperture and concomitant shallow depth of focus, require thin recording media. A number of materials potentially fulfilling this requirement are discussed. These include photoresist-coated metal or semitransparent masks, some unconventional photographic processes, and dyed photographic emulsions. The use of dyed photographic emulsions is recommended on the basis of sensitivity and improved resolution and modulation of the recorded image.

I. INTRODUCTION

In this paper we discuss some recent developments in thin recording media in light of their suitability for exposure in the new step-and-repeat camera system. The requirements of integrated-circuit pattern generation have led to the development of a wide-field objective lens for this camera having high numerical aperture (N. A.) corrected for diffraction limited performance using monochromatic light. Specifically the lens has a 7.1-mm field diameter, $f/1.5$ at 10:1 conjugate ratio, and is corrected for $\lambda = 436$ nm.

This lens has a depth of focus shallower than the thickness of the photosensitive emulsion on the thinnest high-resolution photographic plates. Kodak High Resolution Plates (KHRP) consist of a 6-μm-thick Lippman-type emulsion of small (< 0.1 μm) silver halide grains in gelatin on a flat glass substrate. For any projection lens of f-number less than $f/1.7$ the depth of focus is less than 6 μm. This is illustrated in Fig. 1 which is an idealized ray diagram, drawn to scale, showing in cross section a 6-μm-thick photographic emulsion of refractive index 1.56 into which a linear array of diffraction-limited spots on 1-μm centers have been projected through an $f/1.5$ lens using 436-nm light. Even a perfect lens images a point source as a diffraction patch, the Airy Disc, having a radius r to the first dark ring given by:

$$r = \frac{0.61\lambda}{\text{N.A.}} = \frac{0.61\lambda}{n \sin \theta}. \tag{1}$$

In accordance with this equation, the cone angles (θ) of illumination in Fig. 1 are functions of the lens aperture, the refractive index (n) of the medium, and the wavelength. The width of each rectangular shaded area is equal to the radius of the Airy Disc, and the depth of focus is approximated as the region of overlap of this with the cone of illumination. Light scattering due to the difference in refractive indices of the silver halide and gelatin is not indicated in the figure although it is recognized as a major source of image spread.

From Fig. 1 it is evident that some out-of-focus illumination is capable of acting on the photosensitive emulsion. A fraction of this out-of-focus illumination will be recorded as a function of the sensi-

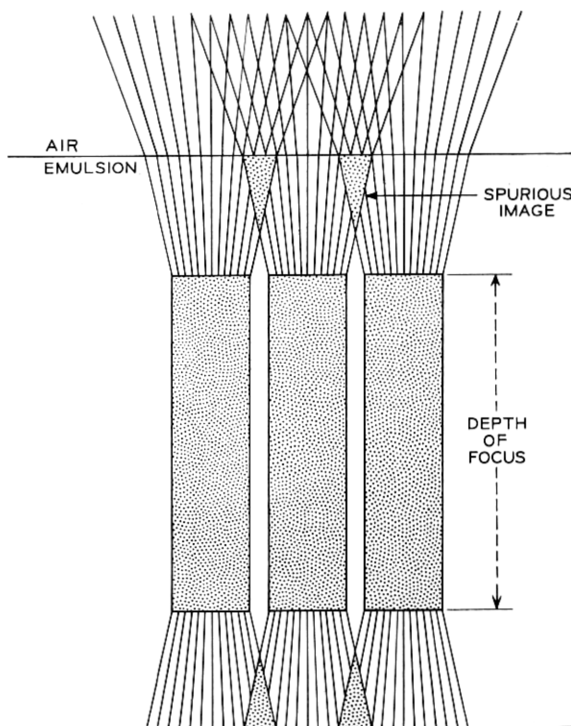

Fig. 1—Ray diagram indicating the depth of focus of a linear array of diffraction-limited spots 1 μm apart projected into a 6-μm emulsion of refractive index 1.56 through an ideal $f/1.5$ lens using 436-nm light.

tivity of the emulsion and the efficiency of the developing process, thus degrading the overall image quality. In the case of large images or uniform-sized small images this could be circumvented by darkroom "clipping" so that exposures below a defined threshold would not be developed. This is not possible in microelectronic photomask production since the intensities of fine lines near the diffraction limit vary as a function of line width.[1] Figure 2 shows the intensity profiles obtained with our 10X lens for isolated lines of widths 1, 2, 4, and 10 μm, all normalized to the same width W. These have been calculated by convoluting the modulation transfer function of the lens at the edge of the field with the light-distribution function of the object, indicated by the dashed rectangle.[2] Since the intensity profiles are symmetrical, only one half-cycle is shown. A focal-plane image of a 1-μm line would have at its center only 69 percent of the light intensity at the center of a neighboring 10-μm line. Thus, "clipping" would result in a loss of fine-line image detail.

Another problem of a depth of focus shallower than the recording-medium thickness is the formation of spurious images. As indicated in Fig. 1, the regions of overlap of adjacent cones of illumination may provide sufficient intensity for exposure giving rise to spurious images between the real images.[3]

Thus, it is apparent that even high-resolution photographic plates must be regarded as three-dimensional systems and for optimum use of the new lenses thinner recording media must be obtained. A number of approaches to the solution of this problem have been tried and are discussed below.

II. THIN PHOTORESIST FILMS

It is immediately attractive to those familiar with microelectronic photolithography to use photoresists, which have demonstrable high-resolution capabilities in thin films, as the required thin recording medium. Figure 3 illustrates this approach using the step-and-repeat camera to project images into a photoresist coating on metal or semi-transparent films on glass substrates. In this case, the thin photoresist film (0.3 μm) records the high-resolution image without depth-of-focus limitations and, after development, controls the transfer of this image by etching into the 0.1-μm film of chromium or iron oxide to provide the optical density and hardness required of a photomask.

However, there are serious problems related to this approach and each of these must be solved before this approach can become prac-

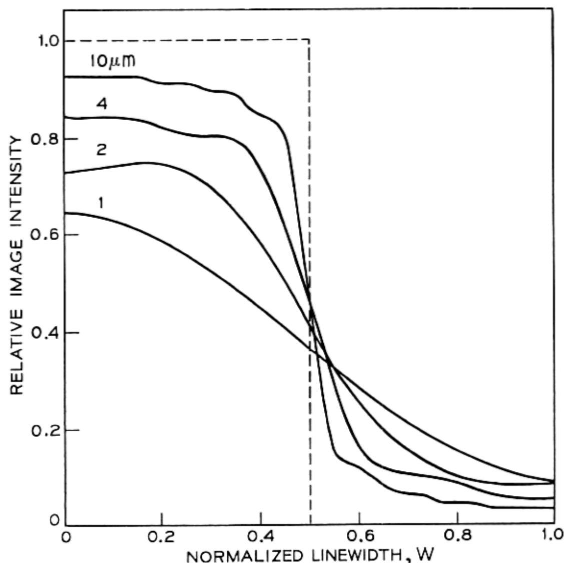

Fig. 2—Calculated intensity distributions as a function of linewidth for isolated slits as imaged by the 10X camera lens.

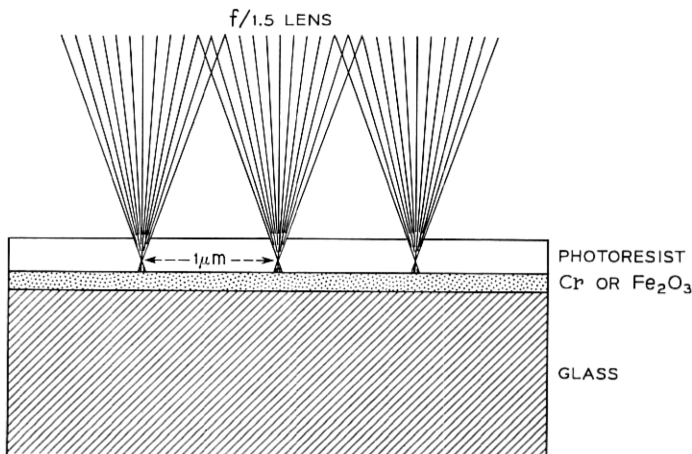

Fig. 3—Ray diagram of projected point sources spaced at 1-μm intervals in 0.3-μm-thick photoresist coating on 0.1-μm-thick film of metal or semitransparent mask material (*f*/1.5 lens, 436-nm light).

ticable. These difficulties are the standing-wave effect due to the reflective substrate, the apparent high-modulation requirements of photoresist, and the low photographic speed of photoresist.

It is known that exposure of photoresist films on reflective substrates leads to the formation of standing waves due to the interference of the incident and reflected light waves, and these in turn produce nonuniformly exposed strata in the photoresist.[4,5] This effect is already seriously detrimental in contact printing with polychromatic light, $340 \leqq \lambda \leqq 440$ nm, and will be enhanced in our projection printing with monochromatic light, $\lambda = 436 \pm 8$ nm. It has been demonstrated that the first node or minimum in intensity lies 0.07 μm above a chromium mask surface so that normal exposure of a negative photoresist in these circumstances would result in a 0.07-μm developed film which is too thin to withstand etching solutions.[6] Recently, semitransparent masks consisting of 0.1- to 0.2-μm films of Fe_2O_3 formed on glass by the vapor-phase decomposition of iron pentacarbonyl have been developed to facilitate alignment procedures during contact printing onto photoresist-coated silicon wafers.[7] The reflectivity of this material is a function of its film thickness but is approximately only 50 percent that of chromium at 436 nm. The substitution of this mask for chromium masks will alleviate somewhat the standing-wave problem. Further improvement will be obtained through the use of darker resists, in which the reflected light will be a small fraction of the incident light.

Recent measurements of the characteristic curves of photoresists (developed film thickness versus exposure, the slope of which is referred to as the gamma of the system) indicate that sharp image-formation requires relatively high intensity modulation in the projected image.[8] Specifically an 80 percent modulation is required for a normally developed 0.4-μm film of Kodak Thin Film Resist (KTFR). This is a stringent demand on the optics of the system since it implies (Fig. 4) a usable resolution in the resist of only 0.18 the limiting frequency of an aberration-free system.[9] Although the use of gentler development conditions and dilute developers leads to some lowering of the constrast requirement,[5] the resolution of this difficulty awaits the development of higher gamma photoresists.

The most obvious limitation of present photoresist systems with respect to their use in a flash source step-and-repeat camera is their low sensitivity. In Fig. 5 the measured values of the spectral sensitivities of four types of photoresist and KHRP are presented. The KHRP sensitivity refers to the reciprocal of the energy necessary in

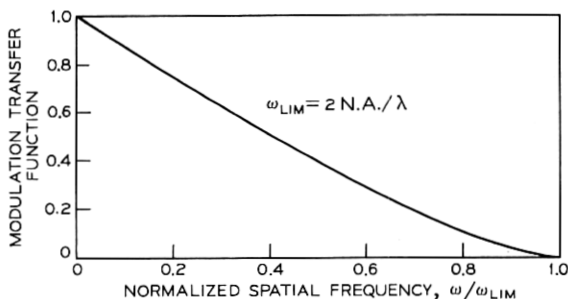

Fig. 4—The modulation transfer function of an aberration-free system as a function of the normalized spatial frequency. ω is the line frequency in cycles per millimeter, and ω_{lim} is the high frequency limit imposed by diffraction effects, a function only of the numerical aperture (N.A.) of the lens and the wavelength of light (λ).

exposure to reach an optical density of 1.5 on development in Kodak type D-19 developer. The measurements on photoresist were carried out using 0.2-μm films of negative resist and 0.5-μm films of positive resist. The box straddling the 436-nm line represents the measured energy output of the camera using type FX-76 xenon flash lamps, manufactured by the EG & G Company of Boston, Massachusetts, and a 15-nm-wide bandpass filter. Obviously, all the resists fall short of the camera requirements and again the need for the development of a new class of resists is implied.

III. UNCONVENTIONAL PHOTOGRAPHIC PROCESSES

There are a number of recently developed photographic processes which would appear, at first glance, to be candidates for the required thin recording medium. It is not within the scope of this paper to present each of these in detail or to analyze their current uses; however, we merely seek to correlate their sensitivity and resolution limits with the requirements of our system. This information is presented in Fig. 6 in the form of a correlation diagram of the measured or reported maximum photosensitivities and resolution limits. The box outline in the center of the diagram serves as the goal with an ordinate range corresponding to the output per flash of the step-and-repeat camera, 50 to 250 μJ/cm^2, and an abscissa range of 250 to 1000 cycles/mm or equivalently 2 to 0.5 μm lines.

Point *A*, for Kodak Plus-X film, is shown merely to relate the scales used to a familiar system having an ASA rating of 125. *B* repre-

sents KHRP with the vertical spread representing the speed difference between plates processed in Kodak D-19 and Kodak HRP developers. C represents a dyed version of the same high resolution plates which will be discussed in Section IV of this paper. Similarly H represents the sensitivity limits of KOR and AZ1350 photoresists at $\lambda = 436$ nm as shown in Fig. 5 together with resolution limits found in contact printing these systems. These serve to summarize the other sections of this paper showing that photoresists fall short of the goal while the dyed plates, with their enhanced modulation, fall within the goal.

Line D represents an interesting extrapolation of the common photo-

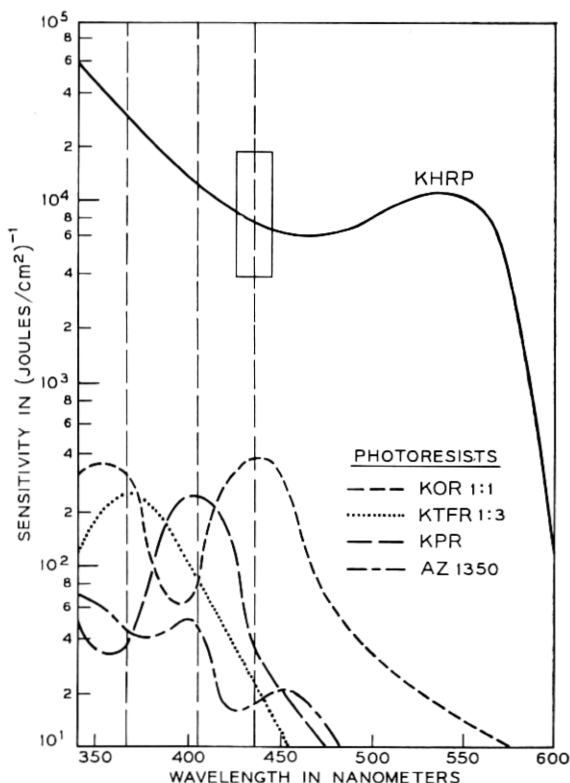

Fig. 5—Spectral sensitivity curves of Kodak High Resolution Plates and some common photoresists. The box about the 436-nm line indicates the reciprocal of the available flash energy range in the step-and-repeat camera. KOR, KTFR, and KPR are photoresist formulations manufactured and sold by Eastman Kodak Company, Rochester, New York; and AZ1350 is a photoresist formulation sold by the Shipley Company, Newton, Massachusetts.

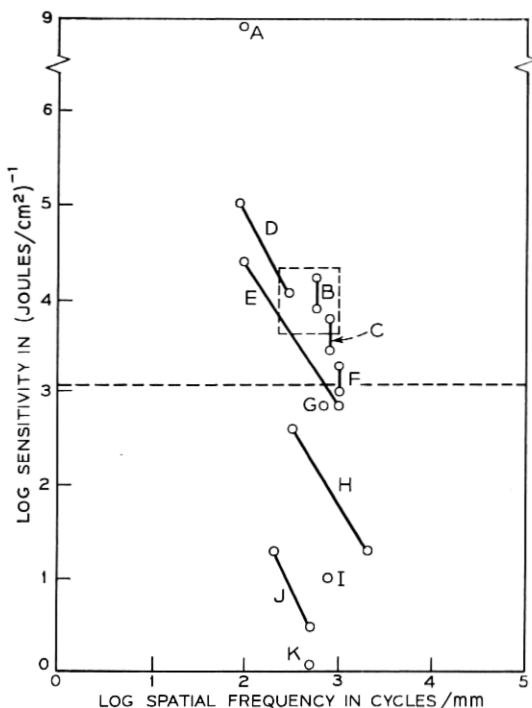

Fig. 6—Sensitivity-resolution correlation diagram showing the target region of the step-and-repeat camera design and the demonstrated performance of a number of unconventional photographic processes identified in the text.

graphic system to its thinnest version, one without the gelatin matrix. This consists of a 0.3-μm film of AgBr evaporated on a glass substrate which, after exposure, may be developed in common photographic developing solutions.[10] While this process does involve amplification and falls within the goal in Fig. 6, it fails as a photomask system because of its very low gamma ($0.3 \leqq \gamma \leqq 1.5$) and its tendency towards infectious fogging on development, i.e., several AgBr grains develop for each exposed AgBr grain.

The line *E* and point *G* represent systems which use photographic physical development as their amplification step. The Philips PD* process is represented by *E* and the Itek RS† process by *G*. [11, 12] The highest-resolution PD-MD1 version of the Philips process does not have the speed necessary for our camera. Neither of these systems is

* N. V. Philips Gloeilampenfabrieken, Eindhoven, The Netherlands.
† Itek Corporation, Lexington, Massachusetts.

at present commercially available in a form suitable for photomask applications.

Another candidate for the appropriate speed range is photopolymerization in which free radical chain propagation steps should provide the necessary amplification. As indicated by *F* one such system has been developed.[13] This is based on the photopolymerization of barium diacrylate to form either an opaque light-scattering image or a clear phase-only image with 0.5-μm resolution. Its speed lies within a factor of five of our requirement; but this data is for a polymerization in aqueous solution approximately 178 μm thick.

In Fig. 6, *I* and *J* refer to organic color-forming photographic systems. The Dupont* Dylux® system *I* develops an intense blue image from colorless precursors on exposure to ultraviolet light; photodeactivation, or fixing, is carried out by exposure to visible light.[14] The "free-radical photography" *J* developed by Horizons Inc.† involves the photochemical reaction of arylamines and carbon tetrabromide leading to a variety of colored images which may be fixed by heating.[15] The resolution capability of each is inherently high because of the molecular nature of the imaging species but their sensitivity is low because they lack amplification steps.* One may calculate the minimum energy necessary to expose at 436 nm a unit quantum yield process to achieve an optical density of 1.0 assuming an extinction coefficient of 10^6 cm^{-1} (the highest known value) for an organic molecule of density 1.0 and molecular weight 300 and result in 0.9 mJ/cm^2. This upper limit to nonamplified photochemical processes is indicated in Fig. 6 by the dashed horizontal line.

Finally, point *K* represents lead-iodide photography.[16] Thin evaporated layers of PbI_2 become transparent when exposed to blue or ultraviolet light at temperatures in excess of 160°C. Similar behavior has been observed in other halides, such as BI_3 and CdI_2, and chalcogenides, such as PbS and Cds. In all cases the sensitivity is very low requiring approximately 1 J/cm^3 for an optical density change of 0.6.

A wide variety of classes of unconventional photographic processes is represented by the above selection, *D* through *K* in Fig. 6, none of which fulfill the requirements of the step-and-repeat camera. This survey does serve to focus our attention on amplified versus nonamplified photographic processes.

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* E. I. duPont de Nemours & Company, Inc., Wilmington, Delaware.

† Horizons, Inc., Cleveland, Ohio.

* Note added in proof. One version of Horizon's system is capable of amplification by photo development, but this produces 0.5-μm grain size.

IV. DYED PHOTOGRAPHIC EMULSIONS

Another approach to the solution of the problem is to utilize thinner coatings of the high-resolution photographic emulsion. However, the suppliers claim that thinner coatings cannot be produced with the same degree of uniformity and quality control. We have suggested that as an alternative approach we need only make the usual emulsion effectively thinner.[17] It is known that exposure of photographic emulsions to ultraviolet light in the region of strong absorption by the silver halide results in images confined to the top layers of the emulsion.[18] This behavior may be duplicated in other spectral regions by dyeing the emulsion such that only the top few microns can be effectively exposed. The focal plane of the projection system may also be confined to this same region by the use of distance pieces or pneumatic gauging which ride on the top surface of the emulsion.

What is required is a nonfluorescent water-soluble dye, strongly absorbing of the exposure wavelength, which may be readily and uniformly imbibed by the gelatin and yet may be subsequently removed in normal processing so as not to lower the overall image contrast. Specifically for $\lambda = 436$ nm, I have characterized three suitable dyes, that is, metanil yellow, tartrazine, and naphthol yellow S. In aqueous solution these have somewhat broad absorption peaks with maxima at 435 nm for metanil yellow, 425 nm for tartrazine, and at 390 and 425 nm for naphthol yellow S. The specular optical density (D) of each dyed plate at 436 nm is a linear function of the weight percent (C) dye in the dyeing solution in the low-concentration region of interest. The molar extinction coefficient and the D versus C relationship for each of the dyes at 436 nm are presented in Table I.

The recommended procedure is to dye the plate by five-minute immersion in a gently rocking solution of C weight percent dye plus 0.02 percent nonionic wetting agent. To maintain the initial plate quality, all solutions are filtered to remove particles larger than 0.1 μm, and the dyeing is carried out in clean hoods equipped with type-1A safelights.

Table I—Dye Absorption Parameters at 436 nm

Dye	E (liter/cm–mole)	Dyed Plate Density (D)
Metanil yellow	2.12×10^4	$11.5C + 0.3$
Tartrazine	1.77×10^4	$1.70C + 0.3$
Naphthol yellow S	1.40×10^4	$3.75C + 0.3$

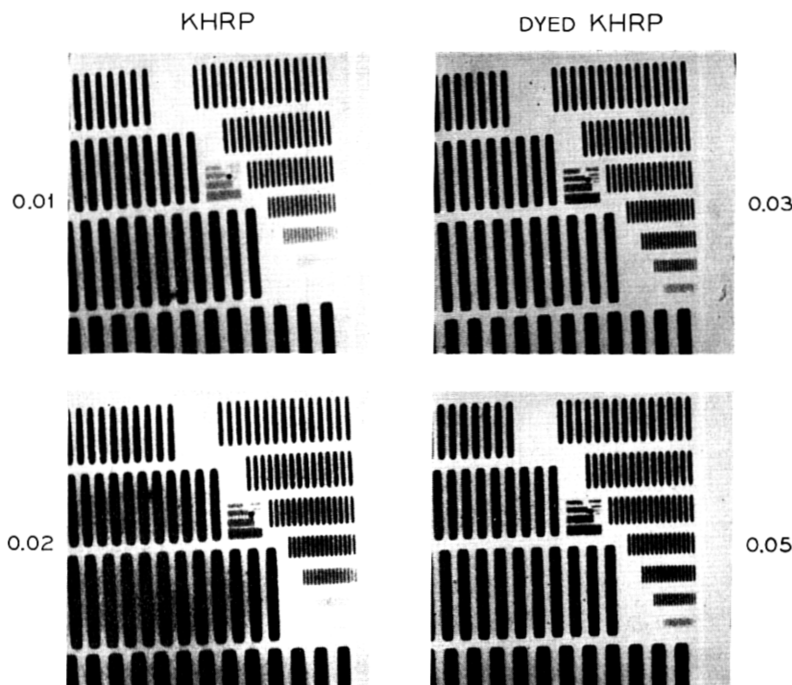

Fig. 7—Photomicrographs of high resolution test target images projected through an $f/1.5$ lens recorded in dyed and nondyed photographic emulsions at the indicated exposure times using 436-nm light.

To characterize the influence of the dye on the photographic response of the plate, monochromatic exposures of a series of plates of varying dye concentration were made through calibrated step tablets. The specular optical density of each step of the developed plates was then measured. The resulting family of characteristic curves for tartrazine-dyed plates indicated that both the speed and gamma, the slope of the characterize curve, of the system decrease with increasing dye concentration. For all further evaluation plates dyed in a 0.2 percent tartrazine solution were selected since their fourfold decrease in speed lies within the exposure capabilities of the step-and-repeat camera. These plates have a specular optical density of 0.64 at 436 nm which is sufficient to eliminate the necessity for an antihalation backing.

A series of exposures of nondyed KHRP and 0.2 percent tartrazine-dyed KHRP were made in a test camera employing the $f/1.5$ lens and 436-nm illumination. Photomicrographs of the results of highest

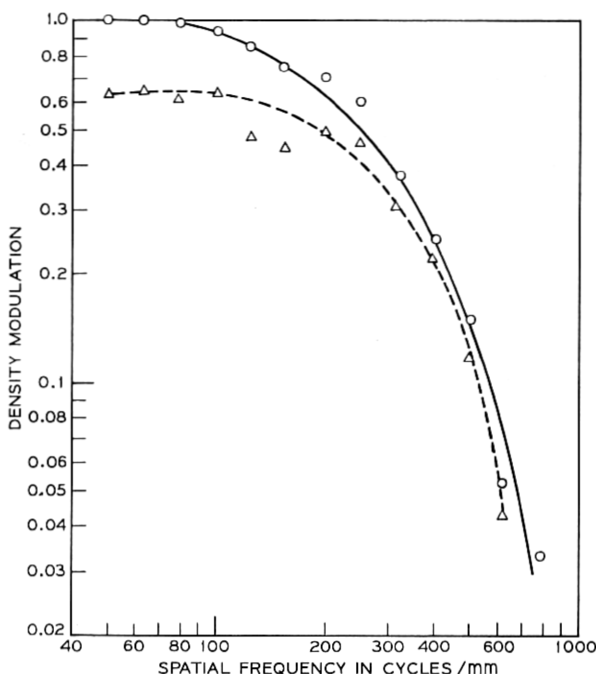

Fig. 8—Density modulation versus spatial frequency of the test images recorded in the dyed plate (circles, 0.05-second exposure of Fig. 7) and the nondyed plate (triangles, 0.02-second exposure of Fig. 7).

resolution are presented in Fig. 7. The bar widths in microns for the eleven 15-bar patterns in the second group on the Ealing* #22-863 test target at 10X reduction are (in the order in which they appear in the photomicrographs, clockwise from 6 o'clock): 5.0, 4.0, 3.15, 2.5, 1.99, 1.58, 1.26, 1.0, 0.79, 0.63 and 0.50 μm. On qualitative comparison the dyed plates appear to resolve finer lines while at the same time providing better modulation of the low frequency bar patterns.

Quantitative measurements of the apparent modulation improvement were carried out on the Ansco Model 4 recording microdensitometer. The 0.02-second exposure of the undyed plate and the 0.05-second exposure of the dyed plate, selected as having the highest resolution on microscopic evaluation, were measured using a 20X, 0.4 N.A. objective with a 5-μm illuminating slit and a 1-μm scanning slit in the microdensitometer. The results are presented in Fig. 8

* The Ealing Corporation, Cambridge, Massachusetts.

in which the density modulation (M) is defined:

$$M = \frac{\bar{D}_{max} - \bar{D}_{min}}{\bar{D}_{max} + \bar{D}_{min}}. \tag{2}$$

The averages were taken over the seven bars and six spaces at the center of each 15-bar pattern. The data demonstrate the improved modulation of the dyed plate at all frequencies plus the slightly higher resolution capability.

The images thus formed in a dyed emulsion were used to control the exposure of a 0.2-μm-thick film of KTFR photoresist by routine contact printing procedures resulting in usable 1-μm lines, demonstrating that the photographic image had sufficient developed optical density. Thus, all the speed and resolution requirements of the camera are fulfilled by these dyed photographic emulsions with the added benefits of increased modulation of low-frequency images and the elimination of the antihalation backing. At the time of this writing, commercial versions of this dyed high-resolution plate are coming on the market.

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