New Ultra-fine Grain Photofilm for Pulsed Colour Holography

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Keywords: **photographic emulsion, silver-halide, colour holography, laser lithography**

Abstract

A new ultra-fine grain silver halide photofilm for pulsed colour holography has been developed. The film is now being manufactured on an industrial basis and is commercially available. The photo-emulsion used has an average silver grain size of 10nm and is sensitive to emissions at 440nm, 532nm and 660nm - the emission wavelengths of the pulsed lasers commonly used in modern digital holographic printers. In the article we present the basic characteristics of the new material.

Introduction

The present article describes the new patent pending photographic material with specific application in holography. It is a new ultra-fine grain ultra-high resolution Silver Halide photosensitive material that exhibits unusually high sensitivity to pulsed Q-switched laser emissions in key regions of the visual spectrum. These materials are particularly useful for full-colour digital and analogue holographic printing and laser lithography.

Key combinations of chemical sensitizing dyes are used to substantially mitigate the usual short-pulse reciprocity failure observed in known ultra-fine grain (high-resolution) materials. In addition, it has been found that minimizing the grain size itself actually mitigates short-pulse reciprocity failure.

Recently pulsed Q-switched lasers producing emissions at 3 distinct wavelengths have been used successfully to make holographic printers which appear free from many of the previous problems associated with the prior devices that were based on CW lasers (D.Brotherton-Ratcliffe et al, WO 01/42861; D.Brotherton-Ratcliffe et al, WO 01/45943; D.Brotherton-Ratcliffe and A.Rodin, WO03/034155). These printers are, in principle, capable of producing, at relatively high speeds, high quality digital 3D holographic images in full colour on flexible substrates such as special photographic films.

Although such machines apparently solve the major problems that have until now frustrated the mass commercialization of digital colour holography, it has been extremely difficult to make photographic emulsions which work effectively with such machines. This is because a photographic emulsion having an extremely fine grain is fundamentally required for the application of colour holography in order to avoid Raleigh scattering in the blue spectral range. However, known ultra-fine grain emulsions suffer from high reciprocity failure and poor visual performance when used with Q-switched laser pulses whose durations are typically of the order of 10 to 100 ns. In addition these latest-generation pulsed holographic printers of course require an emulsion having full colour sensitivity.

The new material solves this problem by implementing a unique Silver Halide panchromatic emulsion that is both ultra-fine grain and yet functions extremely well with Q-switched pulsed laser emissions. Moreover these materials can be and are manufactured in an industrial process.

Review of the development of ultra-fine grain materials

In 1967 N. Kirillov et al. (Russian Preliminary patent application 1026784/23-4) described a general process for the manufacture of Silver Halide emulsions having ultra-fine granules of sizes of <10 nanometers suitable for the recording of holograms by continuous wave laser radiation. The process described therein was based on the hampering of Silver Halide growth by using, in the emulsification process, highly diluted solutions; the emulsion concentration was then increased by applying the method of gradual freezing and thawing. One of the variations of this emulsion is now known as PFG-03C from Slavich – Geola.

Subsequently in 1971 N. Vasiljeva et al. (II SU Holography School, 1971) reported the recording of single-colour holograms on a sensitized emulsion using a continuous wave laser in the red spectral region. An improved red-sensitive dye (with a peak sensitivity at 632.8nm for continuous wave laser radiation and suitable for emulsions which preferably have a grain size of 0.1 micron) was then described by Y. Nakazawa et al. in 1976 (USA Patent 3971664).

The red sensitive dye described in Nakazawa et al. (US Patent 3971664) was then improved in such a way that it became sensitive to pulsed laser radiation (pulse duration – 10^{-6} to 10^{-8} seconds) in the red spectral region (E.F. Klimzo et al, Russian patent 2437389/23-O4, published in 2000). However, the grain size of the silver halide emulsion, for which sensitization using the improved red dye was employed, was 30 and 50 nanometers.

A sensitizing dye for silver halide and silver iodobromide emulsions having grain sizes of 0.1-1 micrometers and sensitive to pulsed laser radiation in the green spectral region (pulse duration – 10^{-5} – 10^{-7} seconds) was described by T. Habu et al. (US patent 4160669, 1979).

Finally, the preparation of an ultra-fine grain silver halide emulsion having a grain size of 5-15 nanometers incorporating sensitizing dyes for continuous laser radiation in all visible spectral regions was described by N. Kirillov et al. in 2000 (Russian patent 2377907/23-4, Russian Preliminary patent application 1026784/23-4).

Summary of the new photomaterial and of its advantages over the other ultra-fine grain materials

Modern digital and analogue holography applications require the use of ultra-fine grain panchromatic materials. However all prior-art ultra-fine grain materials suffer from short-pulse reciprocity failure and high fog levels, making them fundamentally unsuitable for applications involving Q-switched pulsed laser emissions. In addition the prior-art materials exhibit poor holographic fringe contrast when used with pulsed emissions.

The methods of preparation of silver halide emulsions and their sensitization described above are characterized by the emulsions either having silver grains of a size of more than 30 nanometers (Russian patent 2437389/23-O4, 2000 and US patent 4160669, 1979), or by being ostensibly not sensitive to pulsed laser radiation (Russian patent 2377907/23-4, 2000, US Patent 3971664, 1976, Russian Preliminary patent application 1026784/23-4).

In addition there was only one prior-art emulsion (Russian patent 2377907/23-4) that is, at the same time, an ultra-fine grain emulsion with a grain size of 5-10 nanometers and that is also sensitive to all visible spectral regions. However this emulsion is not sensitive to pulsed laser radiation. This emulsion is also very difficult to manufacture in an industrial environment due to the constraint that rapid addition to the gelatin solution of Silver Nitrate and Potassium Bromide solutions is required until a desired concentration is achieved.

We therefore introduce new materials which, when used in conjunction with certain standard known chemical processing schemes, are both ultra-fine grain and are substantially more sensitive to ultra-fast pulsed visible emissions than those known before. In addition the new materials provide for high holographic fringe contrast when a Q-switched pulsed laser is used and also exhibit low fog levels.

The new silver halide emulsion synthesis and its sensitization processes are also fundamentally more technological than those known before (Russian Preliminary patent application 1026784/23-4, Russia patent 2377907/23-4) and thus lend themselves easily to an industrial production. Now the new photofilm can be produced in an industrial way in quantities usually not less than one thousand square meters during one coating of the triacetate substrate base procedure. The new photofilm is currently being continuously manufactured and is freely available from manufacturer in rolls of 1.15m width.

The new film provides all the desired characteristics required by pulsed digital holographic printing machines. These are high diffraction efficiency and clarity of the final holographic image, minimal or controllable emulsion layer shrinkage, good image stability and insensitivity to environmental fluctuations, acceptable sensitivity to the used red, green and blue pulsed laser lines (440nm, 532nm and 660nm), low Raleigh scattering on replay, high emulsion transmissivity both before and after processing, compatibility with existing known chemical processing schemes that can be used in machine film processors, and acceptable material (plate and film) longevity and storage time.

In addition the new photofilm may also be used with CW lasers and may also be used in (pulsed laser or CW laser) holographic copying devices whose function is to copy one hologram to another usually using a single beam which acts both as an illumination beam for the “master” hologram and also as a reference beam for the copy hologram.

The new photofilm may also be used to make general Denisyuk type holograms in full colour, all types of transmission holograms and all types of reflection holograms using both pulsed and CW laser sources.

Characteristics of the new film

- **Spectral sensitization**

Since the emulsion was especially designed for use in conjunction with Geola’s pulsed lasers implemented in its digital holographic printers, the sensitizing dyes were chosen to be close to the said pulsed lasers emitting wavelengths. Thus the maxima of the new film spectral sensitization are at 450nm, 530nm and 660nm. However, as it will be shown below, this does not limit the film to use with Geola’s pulsed lasers only. The film reacts perfectly to other, commonly used CW laser emissions wavelengths as well.

- **Grain size and other physical parameters**

The grain size of the new film was evaluated by its comparison with known emulsions from Slavich – Geola. We have compared the blue pulsed laser light scattering by the known VRP-M, PFG-01, PFG-03M and PFG-03C emulsions coated on the same triacetate substrate as the new film, with the new film. The blue light scattering obtained from the new film was a bit lower than the one from PFG-03C film which is known as having a grain size of ~10nm. Thus we can conclude that the new film has the grain size also of ~10nm. The other photographic characteristics of the film are given in the table 1. The film shows a high contrast level and a good characteristic curve density. This indicates the film’s suitability for laser lithography and for the precise recording of photomasks.

Maximum density on characteristic curve (D_{max})	4.0
Fog level (D_0)	0.1
Emulsion layer thickness (microns)	7 to 8
Contrast	7
Observed life period at 20^o Celsius, 45% humidity.	
Unwinded film roll (months)	18
Rewinded film roll (months)	3
Cut sheets (months)	3

Table 1. Physical parameters of the new film

- **Absorption spectrum**

Figure 1 shows the new photofilm absorption spectrum. The light absorption of the film is relatively small – the film, while observing it by eye, looks clear, but at the wavelengths of the commonly used lasers it shows bigger absorption. That indicates that the film should be sensitive to all the visible light spectrum. Indeed, the holographic recording of diffuse mirrors followed by the measurement of their diffraction efficiency, as discussed below, shows the film's ability to record various colour holograms with high diffraction efficiency.

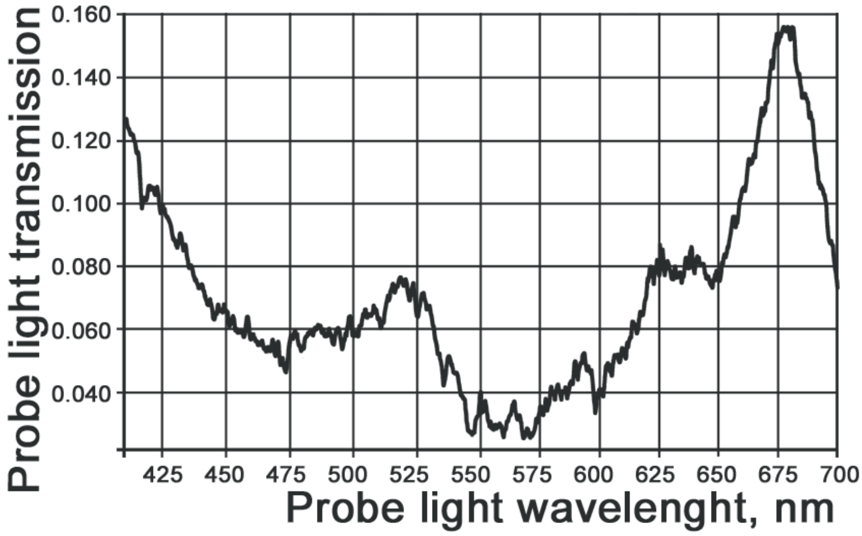

Fig 1. Absorption spectrum of the new photomaterial.

- **Diffraction efficiency**

The diffraction efficiency of the new film was investigated by recording diffuse holographic mirrors using the usual two opposite beams scheme with diffusion of one of the beams followed by its collimation. As a light source we used usual CW lasers with good coherence length (HeNe and Ar) and Geola's pulsed RGB lasers (coherence length >3meters). We have used emulsion from six different batches. The chemical developing of the materials was done with the usual SM-6 developer and PBU-Amidol bleach, followed by drying of the emulsion layer in an alcohol-water solution. Since the emulsion is softer than those with bigger grain size, we needed to harden it before developing. The detailed processing scheme is summarized in table 2. Recipes of the solutions used are given in the table 3. The temperature of all solutions was 21 degrees Celsius.

Exposure:	
Hardening	Hardener, 2-3 min
Wash	Water, 1-2 min
Development	SM-6, 2-3 min
Wash	Water, 1-2min
Bleach	PBU-Amidol until clear (~5 min)
Wash	Water, ~3 min

Drying 1	50%, Ethyl Alcohol
Drying 2	Air

Table 2. Processing scheme of the new film

Hardener	
Formaldehyde	10mL
Water	To 1 litre
SM 6 Developer	
Ascorbic Acid	18g
Sodium hydroxide	12g
Phenidone	6g
Sodium phosphate dibasic If ($12H_2O$)	28.4g; (71.6g)
Water	To 1 litre
PBU-Amidol bleach	
Water	1 litre
Potassium	7.5g
Citric Acid	37.5g
Cubric Bromide	0.75g
Potassium Bromide	15g
Amidol	0.75g
Water	To 1 litre

Table 3: Chemicals used for the new film processing

When processed and dried, the film sometimes shows a replay wavelength shift of ~25nm mirrors towards the blue region of visible light spectrum from the wavelengths used for the recording: i.e., for example when a pulsed laser with the wavelength of 660nm is used, the hologram replay maximum is at 630-640nm. We think that this shift could be controlled by changing the concentration of the Alcohol used for the film drying and/or by using another hardener or bleach.

Parameters	Measured values
Exposure, microJ/cm2	
@ 457nm, CW, microJ/cm2	1250±200
@ 440nm, ~30ns pulse, microJ/cm2	120±20
@ 514.5nm, CW, microJ/cm2	1800±200
@ 532nm, ~30ns pulse, microJ/cm2	330±30
@ 633nm, CW, microJ/cm2	1900±250
@ 660nm, ~30ns pulse, microJ/cm2	550±50
Normal diffraction efficiency for reflection holograms (diffused mirrors), %	
@ 457nm, CW	27.0±3
@ 440nm, ~30ns pulse	14.0±2
@ 514.5nm, CW	35.8±3
@ 532nm, ~30ns pulse	16.5±2
@ 660nm, ~30ns pulse	14.2±2
@ 633nm, CW	38.3±3

Table 4: Diffraction efficiency of the new film

Table 4 summarizes the results of an investigation of the new film’s diffraction efficiency. In the table we have put the exposures that correspond to the highest observed diffraction efficiencies. As it is seen, the diffraction efficiency of the holograms recorded with convenient CW lasers is about twice as large as those recorded with the pulsed lasers. And at the same time, in order to achieve the maximum diffraction efficiency with CW lasers, from 3.5 to 10 times larger exposures are needed. These facts cannot be explained with classic photophysics theories. Since the grain size of the new materials is ~10nm, we think that the energy levels of the silver ion grains and dyes should be taken into account, together with the different conductors’s life times at the particular energy levels. This needs separate investigation.

Conclusions

- A new ultra-fine grain silver halide photofilm for colour pulsed and CW holography is developed and is freely available in industrial quantities
- The film is more sensitive for the pulsed laser radiation than for CW radiation
- Good contrast and low fog level make the new film suitable for laser lithography applications.

Literature

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