

# **The influence of the development in silver halide sensitized gelatin holograms derived from PFG-01 plates**

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## Abstract

Silver halide sensitized gelatin (SHSG) is an interesting technique for the production of holographic optical elements. It combines the high sensitivity of photographic emulsions with the well-known low scattering and high diffraction efficiency corresponding to dichromated gelatin. Owing to the fact that Agfa has ceased production of holographic material it is necessary to find and study new silver halide materials for applications in holography. The differences between these new materials and Agfa material makes it necessary to introduce some modifications on the procedures optimized for Agfa. The influence of the different experimental parameters on the final quality of the hologram is also different when using these new materials. In this work we study the influence of the development step on some holographic characteristics as the diffraction efficiency, the absorption and scattering and the scattered light intensity, for SHSG phase transmission holograms recorded on the Slavich PFG-01 red-sensitive emulsion. We will show that real high diffraction efficiencies can be obtained when using Slavich material for recording SHSG transmission holograms for different developers included in the SHSG procedure. The peak diffraction efficiency reaches a very high level (96% after allowing for reflections) when using the AGFA 80 developer.

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*Keywords:* Holography; Holographic recording materials; Photographic emulsions; Photosensitive processing

## 1. Introduction

Silver halide sensitized gelatin (SHSG) has proven to be a good alternative to dichromated gelatin in the production of transmission holograms. After exposure, the hologram is developed, bleached and then fixed, which creates a latent image by a variation of the degree of hardening of the gelatin [1]. The latent image is amplified by successive isopropanol baths. The main difference between SHSG holograms and common phase holograms recorded on silver halide emulsions, is that the silver halide grains are removed from the emulsion, which serves to increase the diffraction efficiency and lower the scattering.

During the development stage the latent image is formed as a result of a reduction process. After the exposure a latent image is created in the form of a distribution of silver specks. In the vicinity of these specks the developer is oxidized whereas silver ions are reduced to silver, so that an image of metallic silver is formed in the gelatin. The development solution influences the quality of the final hologram through certain factors such as pH (influencing the speed of the reduction reaction) or the concentration of KBr, which prevents the development of unexposed grains. The oxidation products of the developer may also affect the final diffraction efficiency, if they are absorbent. Another important factor influencing the final quality of SHSG holograms is the tanning effect of some developers in the development step. The tanning action of the developer is opposite to the tanning action produced by the  $\text{Cr}^{+3}$  ion, which could reduce the final quality of the hologram.

Investigations carried out by Hariharan on the mechanism of the formation of the latent image in the SHSG processing [2] revealed that oxidation products of the developer can produce a hardening effect on the gelatin when they are put in contact with an oxidizer. This is the case, for instance, of the commonly used D-19 developer, a well-known tanning developer. The high content of sulfite of this developer impedes tanning action during the development step, although a tanning effect does occur during the bleaching step. Weiss and Millul [3] introduced the CW-C2 developer in holographic processes, which seems to improve the signal to noise ratios of the final SHSG holograms in comparison with the D-19 developer. The CW-C2 developer is also a good choice when recording reflection holograms. Simova and Kavehrad

[4] compared the action of two different developers D-19 (tanning) and PAAP (non-tanning) finding that with the non-tanning developer a reduction of the scattering was achieved in comparison with the developer with a tanning action. PAAP gives also better performance than D-19 when reflection holograms are recorded.

These previous investigations concerning the influence of the development step on the SHSG technique were conducted on Kodak 649F and Agfa 8E75 HD plates. But these materials will no longer be produced for applications in holography [5]. However, a currently available range of silver-halide materials has been presented as an alternative to Agfa 8E75 HD. These are the PFG-01 emulsions from the Slavich company. There are some differences between Agfa and Slavich material, such as the degree of hardening of the gelatin and the attainment of a different maximum density which is obtained when amplitude transmission holograms are recorded. These differences will introduce variations with respect to the procedures optimized for Agfa and Kodak emulsions. For instance, the fact that the gelatin of the PFG-01 plates is softer than that of Agfa plates, implies that the final results are more strongly affected by tanning effects in the development step when using PFG-01 plates. In this work we studied the influence of the developer included in the SHSG procedure for transmission holograms recorded on Slavich PFG-01 emulsion, through the introduction of developers of four different types: metol hydroquinone (MQ) developers, ascorbic acid based developers, a catechol ascorbic acid developer (CW-C2), and a pyrogallol based developer (PYRO).

## 2. Experimental

The experiments were carried out on red sensitive Slavich PFG-01 silver halide photographic plates. Unslanted holographic transmission gratings were recorded by using two collimated beams from a 15 mW He-Ne laser (633 nm), with the polarization vector perpendicular to the plane of incidence. The two beams, of equal intensity, incided on the emulsion making an angle of  $45^\circ$  (in air) with each other. With the geometry described, the spatial frequency of the gratings was calculated as 1200 lines/mm.

The exposed plates underwent the SHSG procedure illustrated in Table I, introduced for Agfa 8E75 HD emulsion by Fimia et al [6], so that phase holograms were finally obtained. The gelatin of the PFG-01 is very soft; a high bleach bath temperature could remove the gelatin from the layer, unless it is hardened. In a previous work [7], investigations were carried out on Slavich PFG-01 plates to optimize the SHSG procedure taking into account the degree of hardening of the gelatin of this emulsion. The best results were obtained in two different ways: a) Introducing a hardening bath after the exposure and before the development step, then bleaching the plates at a temperature of 50°C or b) leaving out the hardening bath stage, but instead, maintaining the temperature of the bleach bath at 30°C. In the experiments carried out in this work we chose not to harden the gelatin and the plates were bleached at 30°C. The development stage was modified in order to find the influence of different developers in the SHSG process. Two MQ developers (AGFA 80 and D-19), five developers containing ascorbic acid, a developer based on Pyrogallol (PYRO) and the CW-C2 were used. Table II shows the developers compositions.

The diffraction efficiency  $\eta$  of the recorded phase holograms was calculated as the ratio of the diffracted beam intensity to the incident collimated probe-beam intensity of the He-Ne laser. In order to take into account Fresnel losses and absorption due to the glass substrate, this expression was corrected by multiplying by an appropriated factor [8, 9]. The efficiency of the zero-order or transmission  $\tau$  was similarly calculated as the ratio of the directly transmitted beam intensity to the incident power and was corrected by the same factor.

### 3. Results and discussion

Figure 1 shows curves plotted for the diffraction efficiency as a function of exposure for plates processed using five developers based on ascorbic acid: AAC, PAAC, PAACM, PAACH and PAAP. It can be seen that the best results of the diffraction efficiency were obtained for the PAAP developer, and it is also noticeable that this developer is less energetic than the others, since the corresponding curve is displaced to the left of the others. Figure 2

illustrates diffraction efficiency versus the exposure for four different developers: AGFA 80, D-19, CW-C2 and PYRO.

From these figures we can see that maximum achieved diffraction efficiency was particularly high for plates developed with MQ developers (AGFA 80 and D-19). A high value of 93% (80% if Fresnel reflections are not taken into account) for the maximum diffraction efficiency was obtained for Slavich plates developed in D-19 developer. The zero-order obtained was as low as 0.6%, which implies that the diffraction efficiency was almost the maximum obtainable, the 6.4% remained unaccounted for, having been lost through absorption and scatter. An even higher maximum diffraction efficiency of 96% was achieved for plates developed in the AGFA 80. The zero-order measured for plates developed in AGFA 80 was 2.4%, meaning that only the 1.6% of the incident light remained unaccounted for, lost through absorption and scattering. The higher values of the diffraction efficiency obtained when the Agfa 80 developer was used are due to the high sulphite content in the Agfa 80 developer (100 g/liter), (the sulphite content in D-19 is lower, 45 g/liter). Sodium sulphite inhibits tanning action during the development step. This tanning action tends to work against the differential hardening of the gelatin. Therefore the high sulphite content in the Agfa 80 favours the SHSG process. Adding more sulphite to D-19 should lead to higher values of diffraction efficiency.

For developers based on ascorbic acid (see Figure 1), which is non-tanning, a maximum diffraction efficiency of 79% was obtained with AAC developer with 60 g of sodium carbonate. We also tried to increase the concentration of sodium carbonate to 120 g, but the maximum diffraction efficiency value reached was lower (72.4%). Better results were obtained when the PFG-01 plates were developed in the PAAP developer. The superadditivity effect of phenidone with the ascorbic acid had a beneficial effect and a high maximum diffraction efficiency of 93.5% was achieved by using this developer. The zero order was of 1.8%, and light lost through absorption and scatter was 4.7%. Another developer based on both agents was tried substituting the sodium phosphate and sodium hidroxide of the former by sodium carbonate (PAAC). However, a lower peak diffraction efficiency of 78.2% was obtained. The

addition of a third developing agent was also studied, but diffraction efficiencies were not higher. With the addition of hydroquinone (PAACH) the maximum diffraction efficiency was 73%. And, when metol (PAACM) was the third agent, a maximum diffraction efficiency of 78.7% was obtained.

The use of CW-C2, a catechol ascorbic acid developer yielded a maximum diffraction efficiency of 86.2%, the zero order being of 8.8% and light unaccounted for 5%. This value of the diffraction efficiency is high, but not as high as those obtained by using the MQ developers. The developer CW-C2 is one of the most powerful hardening developers known [1] and its hardening effect is offset by the addition of ascorbic acid (which by the way is essential to this formulation to enable the solubility of the cathecol in the developing solution). Adding more ascorbic acid to CW-C2 should show an increase in tanning inhibition and an increase in differential hardening (modulation) of the hologram. It is important to notice that catechol produces a tanning effect during development, whereas oxidation products of D-19 and AGFA 80 are inert during development and produce the tanning action during the bleach bath.

The other developing agent used was pyrogallol (PYRO developer). But as could be seen from visual inspection (the holograms took on a brownish colour), oxidation products absorbed a large amount of light, which limits the maximum diffraction efficiency obtainable. The maximum diffraction efficiency was of 47.6%, the zero order, 31%, suggesting that a high percentage of the incident light (21.5%) was lost through absorption and scattering. Now the process is dominated by the extreme hardening of gelatin endowed by the oxidation products of this compound. Once that hardening has taken place the differential hardening is wiped out as is seen from the pyrogallol curve.

As mentioned, the highest maximum diffraction efficiency was obtained for plates developed in the AGFA 80 developer. The tanning action is inhibited during the development step due to the high content of sulphite. Now a tanning action caused by the oxidation products of the hydroquinone occurs during the bleach bath, which enhances the hardening action of the  $\text{Cr}^{+3}$  ion, and increases the diffraction efficiency. However, low diffraction

efficiency values were obtained for the PYRO developer due to high values of absorption. It is also interesting to notice the almost flat response of the diffraction efficiency versus the exposure exhibited by PFG-01 plates developed in the PAAP developer over a wide range of exposures. The diffraction efficiency was above 82% for exposures ranging from 100 to 1600  $\mu\text{J}/\text{cm}^2$ .

In order to evaluate the absorption and scatter losses, a percentage as a function of exposure was calculated as  $100 - \eta - \tau$ . In Figure 3, absorption and scattering versus exposure for five different ascorbic acid developers (AAC, PAAC, PAACM, PAACH and PAAP) is represented, while Figure 4 shows absorption and scattering versus exposure for plates developed with AGFA 80, D-19, CW-C2 and the PYRO developer. As can be seen from these figures, the PAAP developer gave the best results and the absorption and scattering was below the 6.2%. The lowest values of absorption and scattering were obtained for plates developed in ascorbic acid based developers. Colorless oxidation products from ascorbic acid after development allows the obtention of low absorbing holograms when using a developer containing this agent. The highest values of absorption and scattering for a developer based on ascorbic acid were obtained for the AAC developer, these values ranged from 2.3% to 12%. The values of the absorption and scattering were higher for plates developed with CW-C2 developer, ranging from 3.1% to 14.3%. Oxidation products of hydroquinone and pyrogallol are light absorbing, resulting in higher values of the absorption and scattering coefficient being obtained for plates developed with D-19, AGFA 80 or the PYRO developer. For D-19 the absorption and scattering ranged from 2.6% to 32%, while for the AGFA 80 from 1.6% to 20.6%. For plates developed with the PYRO developer the lowest value obtained for the absorption and scattering was as high as 9.5% and the maximum value obtained was 24.2%.

Measurements were also made of the scattered light intensity using the setup shown in Figure 5. In Figure 6 it shows the values of the scattered light intensity versus exposure for plates developed with four different ascorbic acid developers (AAC, PAAC, PAACM, PAACH and PAAP) and Figure 7 shows the values of the scattered light intensity versus exposure for plates developed with AGFA 80, D-19, CW-C2 and the PYRO developer.



Figure 7 illustrates that the highest scattering values were obtained for the two MQ developers (AGFA 80 and D-19). This is due to the fact that oxidation products of the hydroquinone contribute to grain growth of the silver halide grains, consequently increasing the light scattered by the final hologram. The values of the scattered light intensity ranged from 3.8 to 90 for the AGFA 80, and from 8 to 60 for the D-19. Low values of scattered light intensity were obtained when the PAAP developer was used, ranging from 2.1 to 22. However for plates developed with PYRO lower values of the light scattered intensity were obtained, ranging from 1.4 to 12.5. This demonstrates that the main contribution to the absorption and scattering coefficient of the plates developed with PYRO is the absorption of light by the final hologram. Table III shows the comparative results for the developers analyzed, corresponding in each case to the value of the exposure which gives rise to maximum diffraction efficiency.

#### 4. Conclusions

We have described the influence of the development step in the SHSG procedure on Slavich PFG-01 emulsion. It was found that the highest values of the maximum diffraction efficiencies were obtained when PFG-01 plates were developed in metol hydroquinone developers (MQ), as high as 96% (after allowing for reflections) when AGFA 80 was used (tanning action is inhibited by the high content of sodium sulphite). Also, good results were obtained when the plates were developed in PAAP developer. The values of the absorption and scattering were below 6% over a wide range of exposures, allowing the obtention of high values of the diffraction efficiency within this region. The worse results were obtained when PYRO was used (a developer with strong tanning action). The results presented here clearly show that tanning effects in the developer, which tend to work against the differential hardening of gelatin, spoil the SHSG process in PFG-01 plates. Our research also shows that good results can be obtained when PFG-01 plates are used in the SHSG processing technique for a wide variety of developers included. The values of the diffraction efficiency achieved were similar to those obtained by the same authors for SHSG transmission holograms

recorded on BB-640 plates [10], with the advantage of using lower exposure values. The high diffraction efficiency and low absorption and scatter obtained for the majority of the developers analyzed, certainly opens up new opportunities with regard to results obtained in experiments with SHSG holograms over the past few years. The results presented in this paper are some of the best reported for SHSG processing technique at the present time for this type of emulsion, and they confirm the applicability of SHSG derived from PFG-01 plates for recording high quality transmission holograms. The results also show that PFG-01 plates are a potential replacement for Agfa 8E75 HD for recording SHSG holograms of high quality.

### **Acknowledgements**

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## Figure captions

Figure 1.- Diffraction efficiencies versus exposure, under Bragg condition for Slavich PFG-01 plates developed with four different developers (AAC, PAAC, PAACM, PAACH and PAAP).

Figure 2.- Diffraction efficiencies versus exposure, under Bragg condition for Slavich PFG-01 plates developed with five different developers (AGFA 80, D-19, CW-C2 and PYRO).

Figure 3.- Variation of absorption and scattering with exposure for SHSG transmission gratings using PFG-01 plates for four different ascorbic acid developers (AAC, PAAC, PAACM, PAACH and PAAP).

Figure 4.- Variation of absorption and scattering with exposure for SHSG transmission gratings using PFG-01 plates for five different developers (AGFA 80, D-19, CW-C2 and PYRO).

Figure 5.- Experimental set-up for the measurement of scattered radiation.

Figure 6.- Variation of scattering with exposure for SHSG transmission gratings recorded on PFG-01 plates developed with four different ascorbic acid developers (AAC, PAAC, PAACM, PAACH and PAAP).

Figure 7.- Variation of scattering with exposure for SHSG transmission gratings recorded on PFG-01 plates developed with five different developers (AGFA 80, D-19, CW-C2 and PYRO).

## Tables

Table I.- Processing schedule.

Table II.- Developers composition.

Table III.- Values of diffraction efficiency, absorption and scattering, and scattered light intensity for Slavich PFG-01 plates developed with different developers for the value of the exposure which yielded peak diffraction efficiency.

**Table I**

1. Develop
2. Rinse in running water for 2 min
3. Bleach for 30 s after the plate has cleared at 30°C
4. Rinse in running water for 2 min
5. Soak in the nonhardening fixer Kodak F-24 for 2 min
6. Wash in running water for 10 min
7. Dehydrate in 50% isopropanol for 3 min
8. Dehydrate in 90% isopropanol for 3 min
9. Dehydrate in 100% isopropanol for 3 min
10. Dry in desiccator for 24 h at 20°C and RH < 20%.

*All solutions are at 20°C except the bleaching step*

**Bleach formula**

<i>Solution A:</i> Ammonium dichromate	20 g
Sulfuric acid	14 mL
Distilled water	1 L
<i>Solution B:</i> Potassium bromide	92 g
Distilled water	1 L

*Just before use, mix one part A with ten parts distilled water, then add 30 parts B*

**Table II**

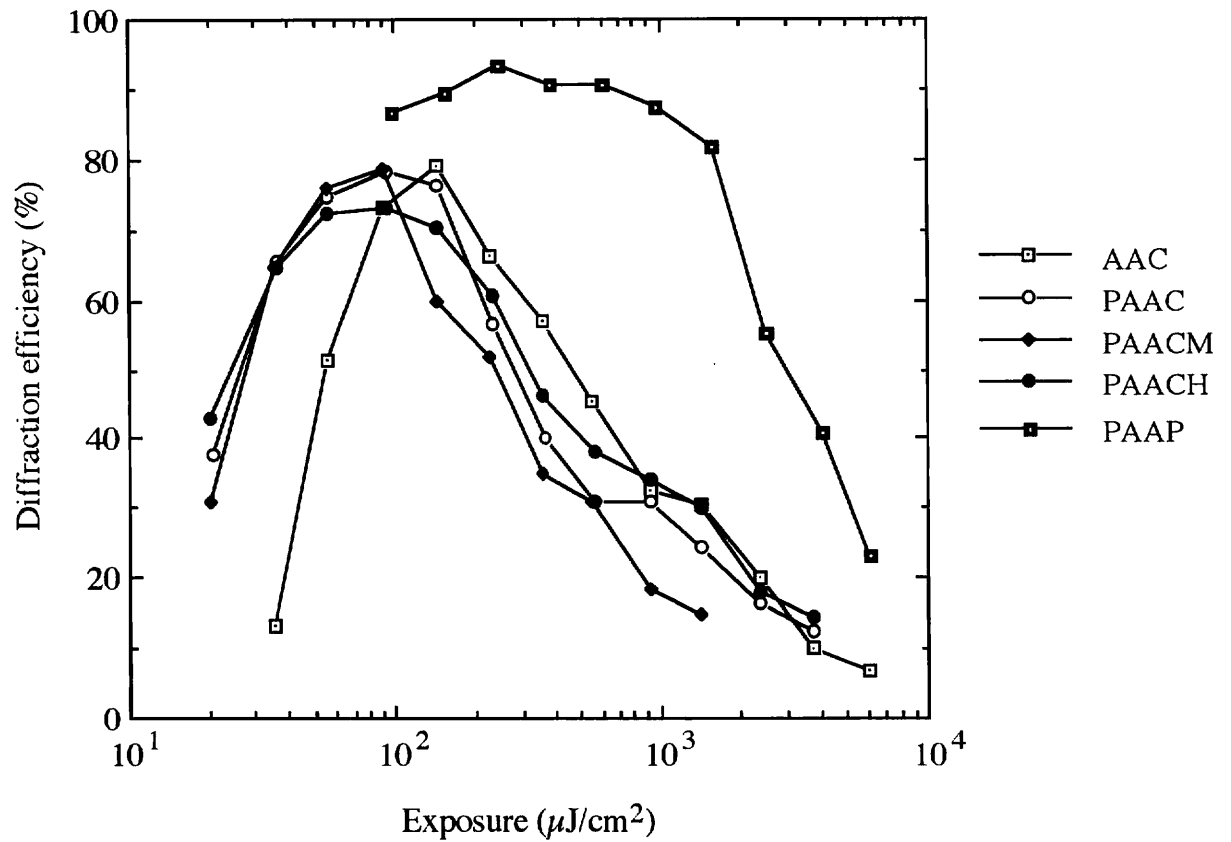
CONSTITUENTS	AAC*	PAAC*	PAACH*	PAACM*	PAAP	AGFA-80	D-19	CW-C2*	PYRO*
Ascorbic acid	18 g	18 g	18 g	18 g	18 g			5 g	
Catechol								10 g	
Hydroquinone			8 g			10 g	8 g		
Metol				2 g		2.5 g	2 g		
Phenidone		0.5 g	0.5 g	0.5 g	0.5 g				
Pyrogallol									5 g
Sodium carbonate (anhydrous)	60 g	120 g	120 g	120 g			50 g	30 g	
Sodium hydroxide					12 g				30 g
Sodium sulfite (anhydrous)						100 g	45 g	5 g	
Potassium carbonate						60 g			
Potassium bromide						4 g	5 g		
Sodium phosphate (dibasic)					28.4 g				
Urea								50 g	
Distilled water	1 l	1 l	1 l	1 l	1 l	1 l	1 l	1 l	1 l
Development time at 20°C	4 min	4 min	4 min	4 min	4 min	5 min	5 min	2 min	2 min

\*Two solutions are mixed just before the development step to form the final solution, one solution containing the sodium carbonate.

**Table III**

	Peak diffraction efficiency (%)	Absorption and scattering (%)	Scattered light intensity (a.u.)
AAC	79	6.4	10.4
PAAP	93.5	4.7	12.4
PAACH	73	5.5	9.4
PAACM	78.7	2.5	9
PAAC	78.2	2.7	8
AGFA 80	96	1.6	6.3
D-19	93	6.4	7.1
CW-C2	86.2	5	7.3
PYRO	47.6	21.5	2





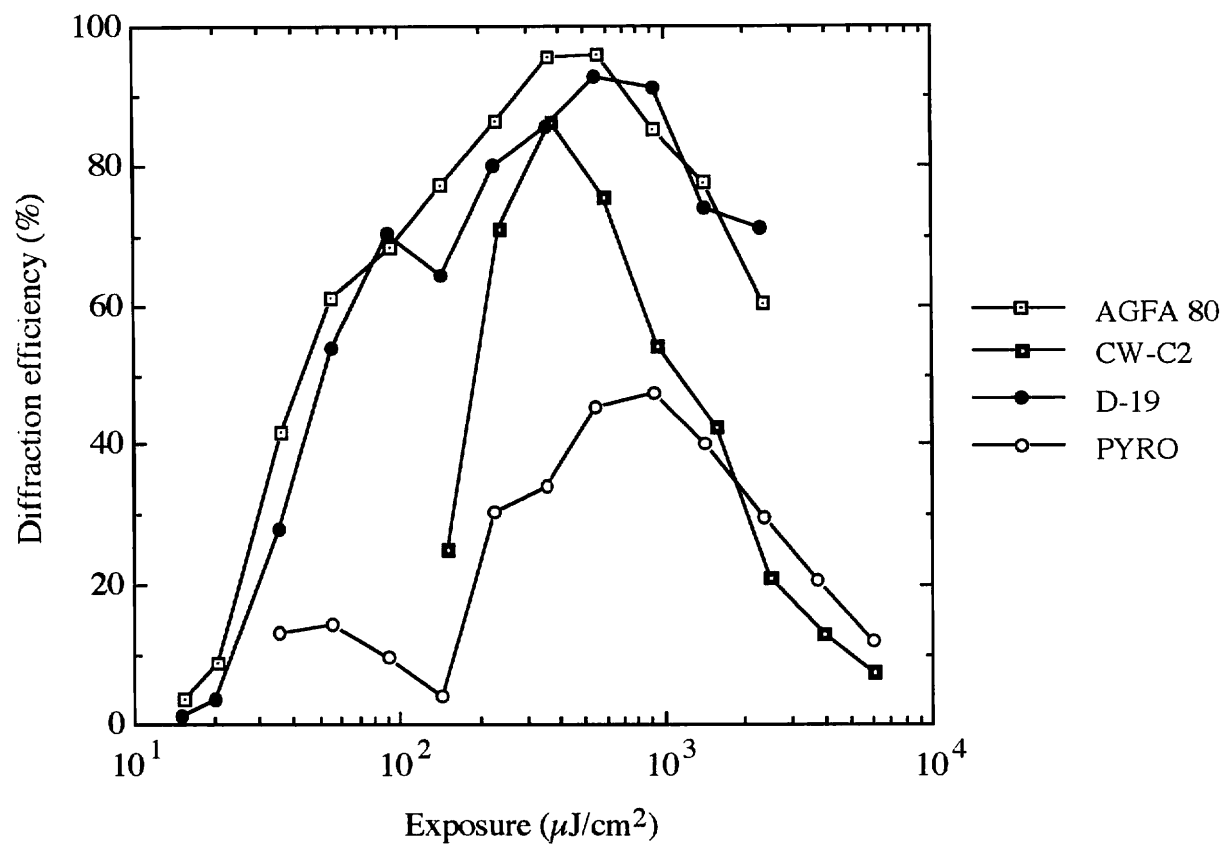
DA 4232

**FIGURE 1**

NEIPP, Cristian; BELÉNDEZ, Augusto; PASCUAL, Inmaculada. "The influence of the development in silver halide sensitized gelatin holograms derived from PFG-01 plates". Optics Communications. Vol. 173, Issues 1-6 (Jan. 2000). ISSN 0030-4018, pp. 161-167

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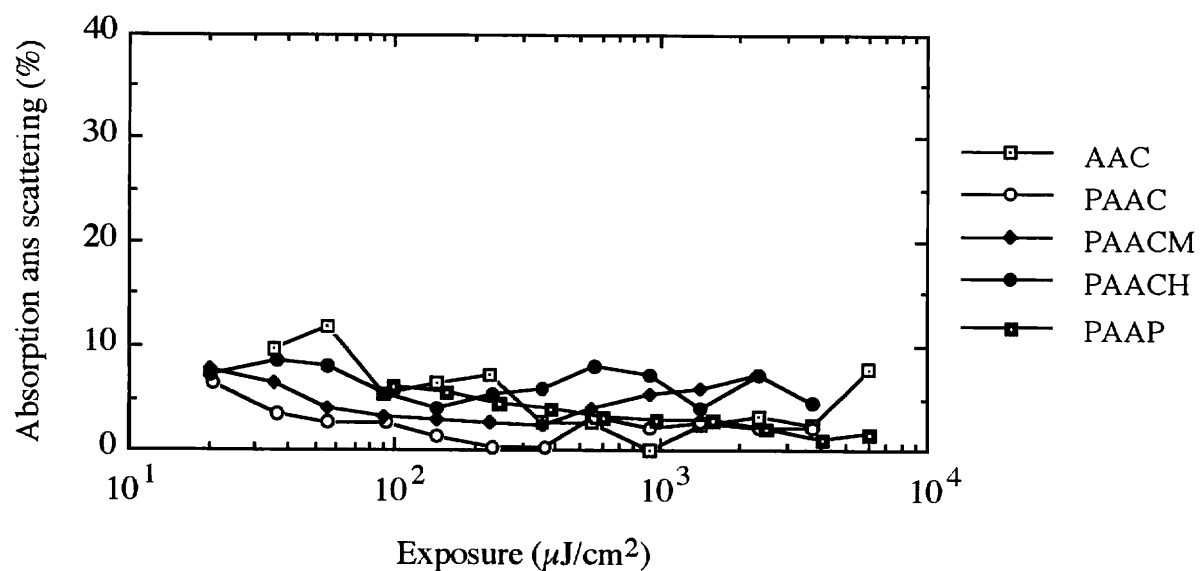
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**FIGURE 2**

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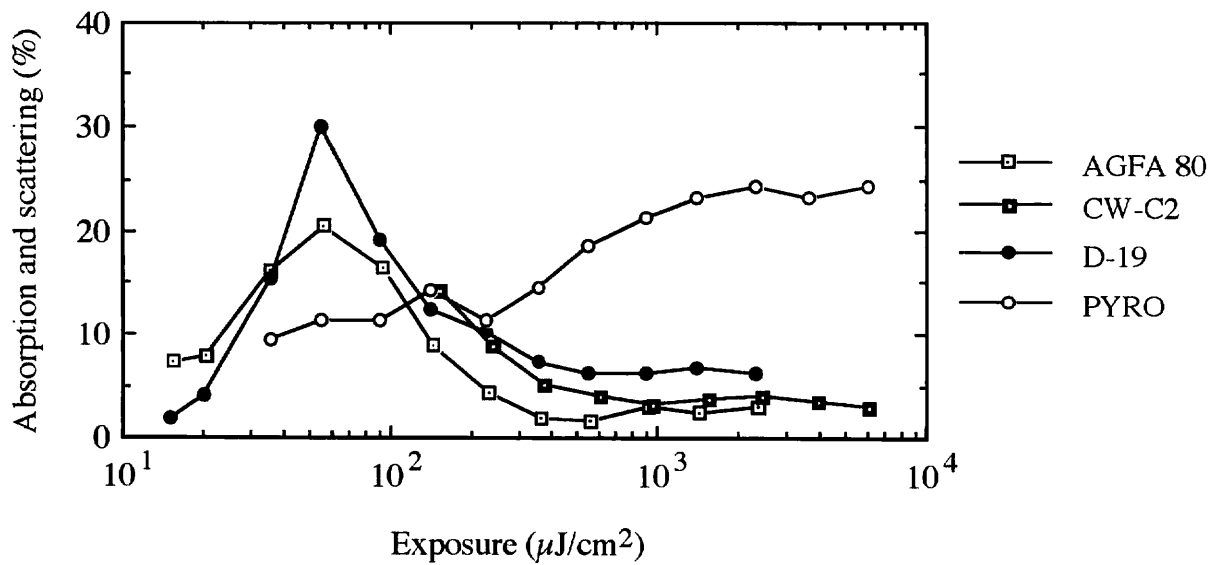
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**FIGURE 3**

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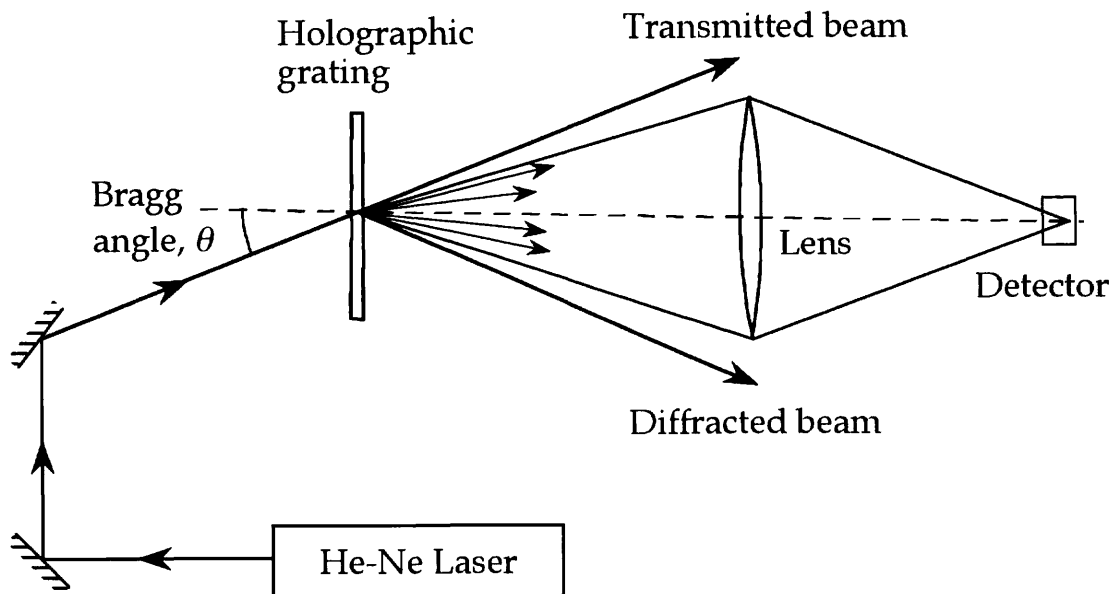
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**FIGURE 4**

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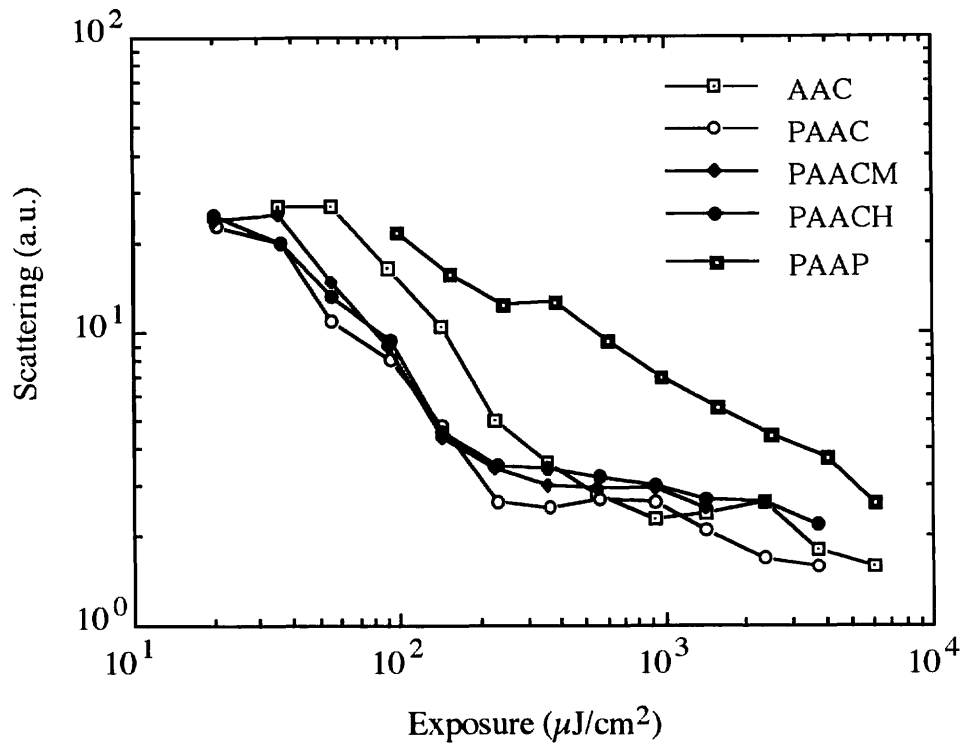
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# FIGURE 5

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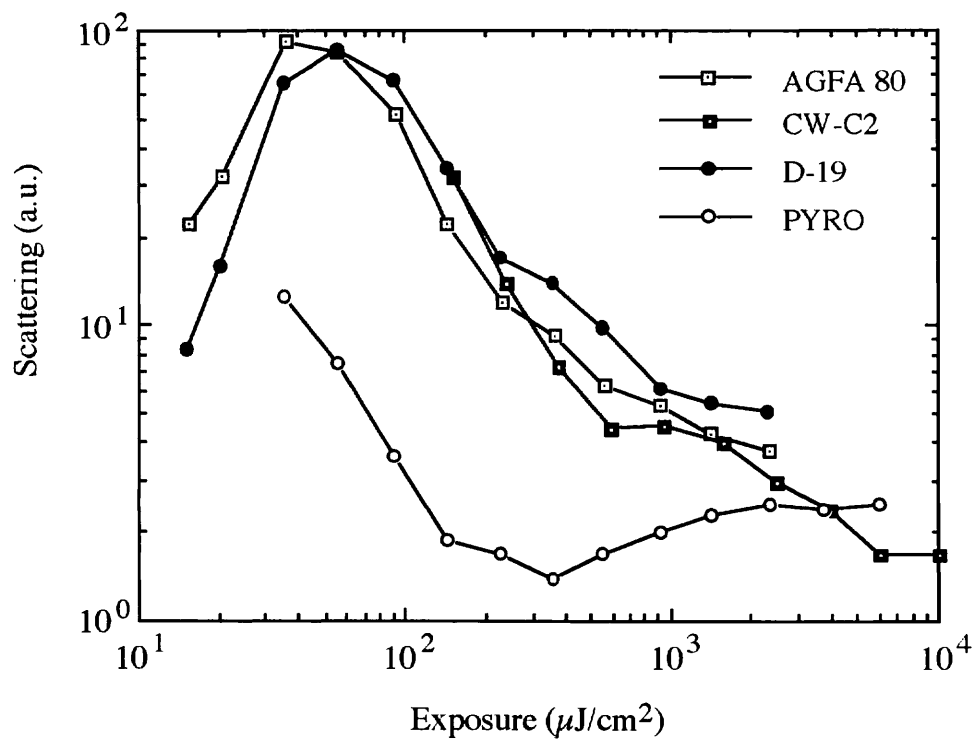
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**FIGURE 6**

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## FIGURE 7

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