

Advances in Holographic Bleaches*

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A survey is given of the results of a large number of trial experiments to evaluate the important requirements of the chemistry applicable to the bleaching of silver halide holograms. In assessing the regimes of bleaching one is faced with a limited range of chemical routes, including methods which produce severe damage to the gelatin and coarse physical grain growth of the silver halide. In this paper we seek to simplify the categorization of bleaches by looking at the relative regimes in terms of (i) the nature of the oxidizing agent, i.e., nominal effective Redox potential and toxicity, (ii) the pH of the solution and the influence of this factor on the quality of the result, (iii) the tendency or otherwise of the bleach to produce physical grain growth (important in reflection holography), (iv) the liberation of stain into the emulsion, and (v) the solvent properties of the bleach in relation to silver bromide. The outcome of some ten thousand trial experiments has produced an apparently unique solution to this problem which we have not been able to reproduce by alternative routes.

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1. Introduction

The bleaching of silver halide holograms has long been a source of difficulty to those who work in the field of holography. In this paper we shall seek to outline the reasons for the main failings of the bleach system and to describe a method which seems to circumvent the main difficulties.

Historically, there are many papers which discuss bleach chemistry. Our own experience is based on more than ten thousand chemical trial experiments on Agfa-Gevaert holographic materials (both red and green sensitive). Both Pennington and Harper¹ and Lehmann et al.² described attempts to solve the main problems, the latter being particularly significant because it leads into some of the more subtle aspects of the practical problem. Following on from this earlier work, mention should be made of the excellent analysis of the phase hologram by van Renesse and Bouts,³ with comments by van Renesse,⁴ and some background work on bleach chemistry by Willems.⁵

Bleaches are notorious for their enhancement of scatter in the image basically because the developed grain is often best left unbleached due to inadequacies of shape and size but also due to the destruction of certain qualities of photographic gelatin and the removal of developer stain. A grain of silver bromide in gelatin is linked to the gelatin host by subtle forces which come into play during coating and hardening and the destruction of this link may well cause a poor interface between the grain and the gelatin host, thus resulting in increased scatter.

We have sought to produce an ideal bleach, but only continual trial experiments and assessment can perfect such a process, and we shall emphasize the great difficulty in associating preconceived theoretical ideas with the practicability of the bleach process. First we shall discuss specific bleach

mechanisms, and then we consider the difficulties encountered in the use of such agents. The pH regime and effective Redox potentials will also be discussed in relation to observed results.

One of the main difficulties of holographic bleaches is their tendency to produce increased scatter by what seems to be granular coagulation of the silver halide, and this problem has also to be overcome in a successful bleach, and depends on the type of gelatin in use on the plates or film.

2. The Basic Bleach Mechanism

Solvent Bleaches. There are two types of bleach in holography: (a) The removal of silver after development by a solvent bleach, and (b) the re-halogenation of silver, usually after a fixer has been applied to the unexposed image (though recent interest has shifted to the no fix regime). Initially we shall concentrate on a bleach of type (a) used for several years as part of the recipe recommended by Agfa-Gevaert for use with their 8E and 10E emulsions:

2 g potassium dichromate
2 ml conc. sulfuric acid
1 l. distilled water

Distilled water is essential since impurities in tap water can seriously upset the action of this bleach and result in unwanted solution of the unexposed image into the bath.

Other agents than dichromate are very damaging to gelatin but sometimes potassium permanganate or ceric sulfate can be used in the same role. The acidic nature of this bath causes gelatin softening which may be very disadvantageous in certain applications such as reflection holography, but otherwise it is useful in cases which require the low scatter left behind in the emulsion due to the removal, both wanted and unwanted, of the halide population.

Experience indicates a maximum of 30% diffraction efficiency on gratings produced by this method. Most developers commonly used in the manufacture of holograms cause some solution of the unexposed grains which may in fact be transferred to the developing silver grains or out into the developing bath. The result of such an action is to deplete the population of unexposed halide so that when a solvent bleach is applied the potential modulation mechanism is weakened. Only if the unexposed halide were to remain unattacked by the developer could we expect to achieve high diffraction efficiency by removal of the silver image and this seems very unlikely as a result of known developer actions. Thus, as an extreme case, the developer ascorbic acid produces a marked solution of the unexposed image and a transfer of the unexposed halide to the developing grain. It seems obvious that such a mechanism followed by solvent bleaching would produce holograms of very low diffraction efficiency and this is substantiated in practice.

These remarks indicate that producing silver by physical transfer to the developing grain is not satisfactory to the holographer, because it will inevitably lead to low efficiency in a solvent-bleached hologram and high light scatter in a hologram in which the silver is converted back to a transparent compound. It is necessary to increase the exposure of the ho-

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lographic plate, thus increasing the number of latent image centers on the grain and encouraging the production of silver from the halide of the grain itself, and not by transfer from the neighborhood.

The rate of reaction for the bleach will vary from one emulsion to another and does depend on how big the developed grains are. It is important to emphasize that bleach chemistry tailored to very fine grain emulsions (c 30–50 nm grain size) may not work with coarse grain material or in cases of excessively hard gelatin (e.g., that of Eastman Kodak 649-F plates).

In general, the silver solvent action is a plausible means of bleaching holograms. However, it is important to note that removing irregular chunks of silver will leave an irregular vacancy in the gelatin host, and the scatter may thus be as severe as if the image were fixed and re-halogenated. To summarize, the solvent bleaches mentioned can be applied without much caution but may lead to disappointment in the achievement of high diffraction efficiency.

Re-halogenating bleaches*

This area of bleaching is probably the one most full of pitfalls and we shall attempt to indicate the major areas of difficulty. Solvent bleaches are perforce highly acidic because the silver complexing mechanism cannot, in general, work at high pH or for $\text{pH} > 2$. The re-halogenating bleach is very different in this respect. The major characteristics to be examined are

1. The role of the Redox potential of the oxidizing agent.
2. The solubility of silver bromide in the oxidizing agent.
3. The tendency of the bleach to induce granular coagulation of the halide or other residue.
4. The pH of the bleach solution.
5. The presence or otherwise in the bleach of free halogen.
6. The speed of the bleach.
7. The tendency of the bleach to damage the gelatin for whatever reason.
8. The tendency to destroy the oxidation products of the developer. Less important are its toxicity and keeping properties.

We shall select certain bleach formulations and discuss these from the standpoint of our own experience. Firstly, we shall examine the formulation of Kodak EB2 (Pennington and Harper 1970)

120 g cupric sulfate
150 g citric acid
7.5 g potassium bromide
1 l. water

to which one adds 3% Hydrogen Peroxide as an equal part just prior to use.

Here, the first and most important aspect is that during the mixing of the bleach, bromine is liberated into the bath due to the nature of the oxidizing agent. Although the Redox potential (Cupric–Cuprous $E_0 = 0.16$ volts) seems to be very small compared to, say, Dichromate ($E_0 = 1.33$ v), the fact is that free bromine is liberated and the bleach process then proceeds as if bromine water were being used. The accelerator (H_2O_2) is a classic example of what has to be used when large grains have to be bleached in very hard gelatin (649F) and is severely damaging to Agfa-Gevaert gelatin. The proportions of (nominal) oxidizing agent and buffer (citric acid) are very high and increase the cost of bleaching. The KBr level is almost immaterial, because once bromine is liberated, the bleach may just as well be bromine water. The presence of large amounts of salts can however, help to reduce emulsion swelling.

Such an uncomplimentary review of a bleach results from the large amount of time spent trying to make this formulation perform well on any image of optical density greater than $D \approx 1$. At higher densities with potentially greater post bleach efficiency, the scatter due to emulsion reticulation and granular coagulation is then usually unacceptable. The pH of this bath is very low ($\text{pH} \approx 2$) and this results in gelatin softening and the risk of physical transfer grain growth effects producing halide clumping and excessive scatter. Results will look bright but usually the scatter makes the hologram very far from the ideal.

We now look at another type of bleach in which a pH independent reaction takes place. This is the type of process involving the agents potassium ferricyanide and mercuric chloride. Both these agents will convert silver to a transparent compound, e.g., silver ferrocyanide and silver mercurous chloride. Examples of bleach constitutions are given by van Renesse and Bouts³ in which either constituent is used singly with a concentration of 10 g/l.

In criticizing these compounds as bleach agents, it is first necessary to comment on the insidious toxicity of the mercury compound, and the danger with the use of ferricyanide in acid conditions in which HCN may be liberated. Both may produce large crystalline precipitates. By their very nature, more than one silver atom is involved per molecule and the crystal growth effects are often disadvantageous. We have been unable to produce results of low scatter with either compound.

Ferricyanide or mercuric chloride may be added to potassium bromide solution with the bromide dominant to produce silver bromide precipitation. The interest in such methods is due to the fact that they can be caused to work over a complete pH range and can possibly produce a hardening effect on gelatin during bleaching.⁶ Again, the crystal growth effects are never satisfactory and surface reticulation of the gelatin also seems to be problematical.

We next consider bromine water. This simple bleach works well with very hard gelatin but has the important disadvantage of destroying the stain of the developer oxidation product. This may be very serious as a problem in relation to light scatter off the finished hologram. Such a bleach softens gelatin and may encourage granular coagulation in anything but very hard samples. Lehmann et al.² added phenosafranine as a desensitizer and found improved results. The actual action of phenosafranine is not just to desensitize the emulsion, since it is also found to reduce dramatically the effect of physical coagulation due to the bleach system, presumably by a blanketing effect. Prebathing holograms in phenosafranine and KBr may produce dramatic scatter reduction with no loss of diffraction efficiency.

Bromine vapor⁷ has been found by us to be very damaging to Agfa-Gevaert gelatin and probably only works with very hard small samples of plate. We have had little success with this method and indeed it is much quicker to dissolve a small amount of liquid bromine in an isopropyl alcohol host, thus producing bleached results in seconds. Again the problem is damage to the gelatin and the destruction of developer stain. The printout stability apparently endowed by this method is undoubtedly due to the trapping of residual bromine in the emulsion layer, so that a reservoir of oxidizing agent exists to replenish the silver bromide population.

There is no doubt that bromine vapor destroys the oxidation products of the developer, and in the important case of a tanning developer will actually remove one of the modulation mechanisms of the hologram, namely the oxidation product shell as outlined in the model of van Renesse.⁸ Thus after the application of bromine vapor the only implicit modulation mechanism that remains is the differential population of halide within the gelatin structure (i.e., regions of coarse grains and regions of fine grains), and the image quality of holograms in which this is the primary mechanism of modulation is usually unattractive due to the disadvantageous

* Including bleaches which convert silver to an arbitrary transparent precipitate.

light scattering properties of the re-halogenated developed grains. In this context it is important to note that the ferricyanide bleach discussed in this paper is also destructive of the developer oxidation product, and for this reason will annihilate the tanning modulation produced by certain developers.

At this stage we consider whether other halides can be used as the precipitating agent. The use of potassium chloride as the alkali halide is usually unsatisfactory because AgCl is strongly soluble in KCl, and thus during the course of bleach action a considerable loss of image occurs into the bath. There is no doubt that the crystal structure of AgCl is advantageous in terms of light scatter but printout is a very severe problem. We have produced AgCl images by the use of in-bath phenosafranine, but the efficiency is always low. Potassium iodide may seem to offer the advantage in that AgI should be relatively free from print-out, and by having greater polarizability the efficiency of the hologram should be higher for a given population density of the halide. In fact, it is difficult to produce the correct conditions for fine AgI crystal growth, and for most applications the results are unsatisfactory.

Many exotic methods were tried with much success. We should mention here the interesting work of Willems⁵ on the use of organic accelerators to overcome the bleaching difficulties of persulfate, which, although having a high available Redox potential, suffers from a serious double-layer effect at the silver grain due to the negative charge on the oxidizing ion. The use of the dye "Bindschedlers Green" is interesting in its role as a bleach accelerator but impractical due to cost and stability.

In trying to arrive at a solution to the problem, our first successful method consisted of using the oxidizing agent ferric nitrate together with KBr and phenosafranine. At the time we did not fully understand the anticoagulant role of phenosafranine and merely invoked its use as a printout inhibitor. Our information consisted of

100 g ferric nitrate
30 g KBr
0.3 g Phenosafranine
1 l. water

Such a bleach is effective but it does leave iron stain in the gelatin and in fact liberates bromine into the bath during preparation. The level of KBr concentration is very important, since above 30 g/l. there is a risk of coagulation effects on the grains, probably due to the overall solubility of AgBr in this bath. Results can be tolerably efficient with grating diffraction efficiencies as high as 50-60%, though with more sophisticated developers than those used by us at the time,⁹ these levels can probably be exceeded.

In criticizing the above formulation with hindsight, one can object to its acidity and tendency to soften gelatin and the excessive amount of oxidizing agent (ferric nitrate) required in its constitution. The pH regime is perhaps its most serious drawback and no bleach should be knowingly permitted to soften gelatin.

3. A Working Solution to the Bleach Problem

After many thousands of trials, a method has been found that is simple and effective and works well for both transmission and reflection holograms. This method has the following advantages

1. It is simple and requires small amounts of chemicals in its formulation.
2. The pH is adjustable in the range 1-9.5.
3. The release of free bromine into the bath is largely inhibited.
4. It does not destroy developer stain.
5. The pH can be adjusted so that gelatin is hardened rather than softened by the bleach.
6. The solubility of AgBr in the bleach solution is very low

and the concentration of KBr can be controlled to suit the gelatin of the coating.

Essentially a bleach must convert a grain of silver into a grain of silver bromide without altering the shape and size of the grain (or at least not producing irregular coagulation) and also without destroying the interface between the grain and the gelatin host. Such requirements are very specific and we have only found one solution to the problem.

The first point to note is that the developer produces an oxidation product blanket around the grain (usually of a quinone type of structure) and that this product may well be of the type that can interact with the gelatin and at the same time attach itself to the grain. Such substances are produced in particular by tanning developers of which hydroquinone, catechol, and pyrogallol are examples. We regard this blanket as having the power to optically match the grain to its host by either reducing scatter through brown stain or acting as a clear index matching layer. The blanket is easily destroyed in the case of bleaches containing free bromine and the grain can then be left naked in its host structure. Our experience shows that the optical scatter increases considerably when this destruction takes place.

To control optical scatter after bleaching effectively, we have found it preferable to avoid the destruction of the oxidation product. We note first that a quinone exists, i.e., *p* benzoquinone, which (by virtue of its family likeness to the oxidation products of the phenolic developers) should not destroy the oxidation product shell around the gelatin. This substance has a molecular structure as below



It is one of the simplest organic oxidizing agents. It is toxic both by inhalation and swallowing and must be treated with more care than its associated developing agent, hydroquinone. We shall henceforth use the abbreviation P.B.Q.

We have constituted a bleach as follows

2 g P.B.Q.
30 g KBr
1.5 g boric acid
1 l. distilled water

This bleach does not keep indefinitely but has almost ideal properties. *It should be regarded as toxic and the vapor is best kept well removed by adequate ventilation.* The pH is set at about 5 by the inclusion of the trace of boric acid. One can scarcely denote the acid a buffer since it is very sparingly soluble.

We have found that the "buffer" is crucial and that a properly buffered solution (e.g., with KOH and an acid) is not as desirable as the formulation above. All correctly buffered solutions seem to increase surface reticulation of the gelatin or even induce scatter by coagulation. The KBr level is important and excessive values will lead to coagulation of the grains and increased scatter. Thus with hard gelatin, 50 g/l. may be tolerable but with soft gelatin 30 g/l. is a safe limit. There is no doubt that the general problem of coagulation is linked to the hardness of the gelatin and its physical transfer characteristics.

P.B.Q. is well known as a bleach in old photographic papers produced before the turn of the century. Thus Lumières and Seyewetz had established that it hardens gelatin in increasing amounts as the pH of the bath increases.

When the developer in use does not harden gelatin itself, it may be of advantage to buffer the bleach with Borax to which a little dichromate is added as an accelerator. Thus the formulation

30 g KBr
15 g borax
2 g potassium dichromate
1 l. distilled water

to which 2 g P.B.Q. is added just before use, is very effective when used with a developer like Neofin.⁹ Such a bleach is of transient stability with a life of about 15 min, but produces very low scatter results and undertakes its own tanning effect.

The boric acid buffered bleach is the most satisfactory composition that we have discovered. The results are so good that competitive bleach formulations (which might for example be more stable) have not been found despite exhaustive attempts.

The advantages of the simple boric acid buffered mixture are: (a) It has a low tendency to produce enhanced scatter by coagulation; (b) it hardens or at least does not soften the gelatin; (c) it does not destroy developer stain; and (d) it produces results of very high diffraction efficiency due to very precise bleaching without transferring the halide from one place to another in the gelatin.

Recent trends in development have favored the use of fixation-free methods and this is preferred as a means of reducing surface relief effects that usually accompany fixing before bleaching. We have found that reflection holograms developed in Pyrogallol are especially well treated by our organic bleach since gelatin collapse is completely inhibited except in the case of excessively soft gelatin.

Transmission holograms are particularly effective when bleached in P.B.Q. and the developer is chosen to give just the right degree of stain to reduce optical scatter.

We recommend physical transfer development so that no fixing is required. Results for the diffraction efficiency of simple two-beam gratings are shown in Fig. 1, using a new developer produced by Agfa-Gevaert. The materials used were Agfa-Gevaert's 8E75 HD film and 8E56 HD plate. Results of efficiency versus prebleach optical density measured at 633 nm are shown below. In these cases the efficiency has been defined as the ratio

$$\eta = \frac{\text{Intensity of diffracted light (not including zero order)}}{\text{Total intensity of transmitted light}}$$

This does not allow for scatter, attenuation, or front face reflection but is certainly meaningful in practice. With the modulation index attainable by this chemical method, a problem arises with narrow inter-beam angle recordings as multiple orders are generated with high efficiency. We have not yet investigated this nontrivial problem, which involves all the difficulties associated with the theoretical aspects of frequency modulated carrier waves at high modulation index.

The final outcome of this work may be summarized by the conclusion that for visual display holograms it is vital that a degree of stain be left in the hologram so as to reduce the subjective effects of scatter. A stain-free hologram may have objectionable opalescence which strongly degrades image contrast. It is clear from the experimental results that a stained hologram will attenuate the input wave to the hologram but that the effects of scatter can be relieved by sacrificing some of the input wave intensity on playback. If the grains are "cleaned" by a de-staining bath, then the opalescence effect is always objectionable even with materials at current production limits of 30 nm grain size. The transmissivity of a "cleaned" transmission grating with the image developed to the optimal density $\bar{D} = 2.5$ is only about 85%, and allowing for front face reflection probably means that about 10% of the light is scattered. The authors are of the opinion that for transmission holograms, where stain can be objectionable if too dense, the final drying stage of the hologram is then important. We have noted that stain tends to increase in the first few hours after drying and we have not ruled out a type of printout effect which liberates colloidal (red) silver. A reduction of grain size to a 15-nm mean would greatly alleviate this problem and possibly allow us to work with unstained (or much more lightly stained) holograms. Alas the

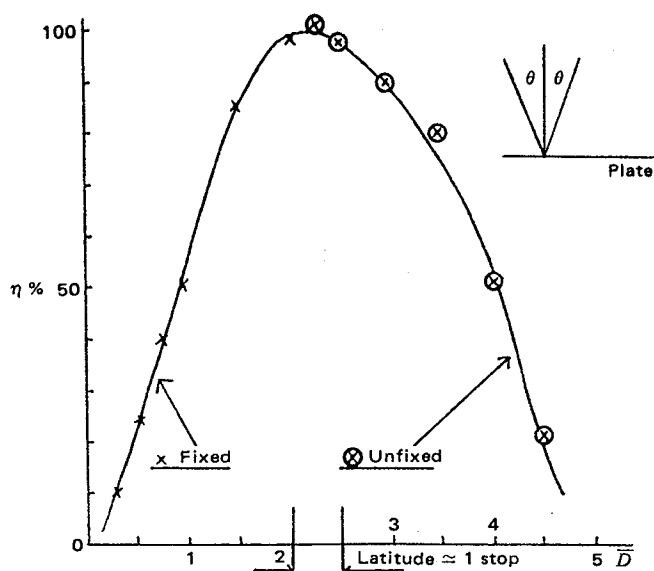


Figure 1. The diffraction efficiency of Agfa emulsions 8E75 and 8E56, for recording at 633 nm with $\theta = 25^\circ$ (recording geometry as illustrated).

trend toward silver halide with the sensitometry of dichromate is obvious.

4. Conclusions

The method outlined in this paper is an empirical solution to a frustrating problem. The results clearly depend on the correct choice of photographic emulsion. It should be noted that for an emulsion with a Gaussian grain size (x) distribution of the form

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} \left[\exp \frac{-(x - \mu)^2}{2\sigma^2} \right]$$

then the mean Rayleigh scatter cross-section which depends on x^6 is of the form

$$C\mu^6 \left[1 + \frac{15\sigma^2}{\mu^2} + \frac{45\sigma^4}{\mu^4} + \frac{15\sigma^6}{\mu^6} \right]$$

where C is a constant. Thus in white light holography, the use of an emulsion with large spread σ can lead to serious scatter. The above result also indicates the care which must be taken in the development process to avoid large irregularly shaped developed grains. We recommend Agfa-Gevaert 8E75 HD and 8E56 HD emulsions with nominal $\mu = 30$ nm and $\sigma = 5$ nm.

Given that the original emulsion itself is not opalescent to any significant degree, the organic bleach leaves the hologram with remarkably low scatter and high efficiency. It cannot be assumed that this method is the only satisfactory solution to the problem, but much frustrating experience has failed to discover an alternative comparable in all the required aspects.

Since our work, the important paper of van Renesse⁸ has highlighted the subtleties of the light scattering problem associated with the conversion of the silver image to a transparent compound of silver. As a result of his work we again looked carefully at the possibilities of ferricyanide type bleaches being more advantageous than the brominating system recommended in this paper. In practice we have found that simple ferricyanide bleaches cause reticulation of the gelatin and thus if some form of surface index matching adhesive is not used on the hologram, scatter can be profound from relief origins. In the manufacture of large display holograms this would be a serious drawback and would not encourage us to invoke the low light scatter properties of silver ferrocyanide in the final hologram. This does not imply that

either van Renesse is incorrect in his assertions, or that it might not be possible to adjust the chemistry of the ferricyanide bleach to alleviate the reticulation difficulty. Such adjustment would, however, be very subtle and require much research.

Our global view of the conversion process of silver to a transparent compound would certainly emphasize that the growth of coarse grains in bleaching is associated with the solubility of the silver compound in the medium of the bleach bath. Recent results have indicated that it is possible to vary the crystal growth regime through very fine to very coarse precipitation, and that in practical terms it is not possible to state that the light scattering properties of one or other precipitate is to be preferred, since the specific bleach chemistry may well lead to a coarse grained precipitate of a medium which has inherently advantageous theoretical light scattering properties along the lines outlined by van Renesse.

In conclusion, we would simply point out that a practical working bleach must not lead to side-effect difficulties which greatly increase the technological problems after the bleach is applied. The *p* benzoquinone method is designed to give

easy success in the bleaching of silver holograms but it is to be emphasized that the remarks in this paper simply provide some guidelines and only scratch the surface of this complex problem.

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