

## Dichromated gelatin — some heretical comments

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### ABSTRACT

This paper looks at some ideas old and new that relate to the formation of images in dichromated gelatin. The traditional view that the dichromated system hardens gelatin thus preventing solubilization of the material must be balanced against other observations such as that of the reduction of the bulk index of the gelatin layer and the appearance of gelatin in the processing solutions. We revisit the problem and take a look at some new chemical ideas that relate to the behaviour of gelatin during bleaching of silver halides. A new method for the processing of silver halide-sensitized gelatin (S.H.S.G.) is proposed which endows the silver halide emulsion with more than three orders of magnitude of speed when compared with D.C.G. per se.

### 1. INTRODUCTION

The subject of dichromated gelatin as a recording medium for holograms has received enormous attention over the years due to the importance of the medium to the manufacture of heads-up displays for military and latterly civilian cockpit applications in aeroplanes and motor vehicles.

Dichromated gelatin (D.C.G.) is a complex structure involving care and consistency with the recording and processing technique in order to exploit its full potential. **It is not possible to give a full bibliography of the subject since much important Soviet work has remained buried due to their needs of classification and just general lack of communication.** In the West, the important contributions of Shankoff<sup>1</sup> and Chang<sup>2</sup> amongst numerous other workers cover key details of the process. Much interest has of late centred on hybrid techniques in which silver halide layers are converted to pure phase modulated gelatin revisited later on in Figure 4, using subtle process techniques. We should perhaps single out the work of the Spanish group under Fimia<sup>3</sup> in this area of activity which builds on early developments by Chang and co-workers<sup>4</sup>, Graver *et al*<sup>5</sup>, Angell<sup>6</sup> and others. Silver halide-sensitized gelatin (S.H.S.G.) essentially combines the high signal to noise possibilities of D.C.G. with the high innate light sensitivity of the silver halide materials. There are however serious penalties to pay when one extracts salts of silver from a gelatin layer, the most important being the collapse of the Bragg structure and the need to find some finishing method of 'propping up' the voided material. Scatter may not indeed be as low as desirable due to the fact that silver halide when removed leaves voids in the gelatin which themselves act as scattering centres.

The purpose of this paper is to provide some food for thought in the background to the process for D.C.G. and S.H.S.G. We shall look at a number of key laboratory observations based upon the study of the silver halides that pose important and as yet only partially answered questions. We do not offer an entirely new route to the manufacture of D.C.G. at this stage but the way is left clear for a range of detailed studies that may ultimately enable us to replace D.C.G. as such with new chemical formalisms and processes.

What we propose in this paper is that the large values of index modulation observed in D.C.G. are plausibly caused by gelatin hydrolysis in the nodal parts of the image structure. If the collapse of the recording layer can then be reversed or inhibited, void modulation occurs, ranging between the refractive indices of gelatin (augmented by added Chromium) and air.

We structure this paper by first spelling out what are seen as a set of key observations in the laboratory. These are then collated to provide guidance for a further understanding of the D.C.G. and S.H.S.G. processes.

Whilst there is no disputing the hardening of gelatin by dichromate, we must add to this the observation that dichromate bleaches used in their rehalogenating or solvent form on the silver images can cause layer softening and disruption of the images.

## 2. KEY LABORATORY OBSERVATIONS THAT RELATE TO THE IMAGE FORMING MECHANISM OF D.C.G.

(a) Major solvent bleach agents for silver are capable of disruption of gelatin layers.

Here, we observe that the removal of developed silver by a solvent bleach in order to provide modulation of a silver halide hologram can cause the disruption of the gelatin layer.

We specify such solvent bleaches as belonging to the class of chemicals shown below; their ionic Redox potentials accompany them.

Sodium Dichromate	
Potassium Dichromate	1.33 Volts — low pH conditions
Ammonium Dichromate	
Pyridinium Dichromate	
Potassium Permanganate	1.65 Volts — low pH conditions

The dichromate family and permanganate all exhibit large redox potentials which enable their corrosive ability when attacking silver in a gelatin layer. By comparison, we have an odd man out of low potential:

Cupric Sulphate	0.16 Volts
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To this family, we have recently added new combinations:

Ferric Sulphate (or Nitrate)	0.77 Volts	and	Dichromate
+ Potassium Persulphate	2.00 Volts		+ Persulphate

These unusual combinations rely on the intrinsic oxidising power of the Ferric and dichromate compounds together with the regeneration of the reduced form of these compounds (as a result of attacking silver metal) back to their original form. Potassium Persulphate itself cannot attack silver strongly despite its large redox potential because of a charge barrier problem that prevents close proximity of the Persulphate ion to the silver site. However, Persulphate can be used to regenerate (or oxidise) other compounds in common solution. Bjelkhagen, Phillips, Wang<sup>7</sup>.

We have compounded novel silver solvent bleaches as follows:

Ferric Nitrate	100 gm	Ammonium Dichromate	10 gm
Potassium Persulphate	20 gm	and Potassium Persulphate	20 gm
Distilled Water	1 Litre	Potassium Hydrogen Sulphate	2 gm
		Distilled Water	1 Litre

These solutions will remove silver from a developed layer. Their pH is low due to the acidity of the Potassium (or Sodium) Hydrogen Sulphate or the Ferric Nitrate. Rates of silver solution can be controlled much more sensibly than with the usually over-rapid dichromate formulations. We should perhaps note that pH control of the Ferric bleach has not been attempted (say by a higher pH buffer) but may be important.

In the dichromate bleach, the rate is controlled by the lowered acidity and regenerative action of the Persulphate. The ionic lifetime of  $\text{Cr}^{3+}$  ions is directly controlled by the regenerative process.

We demonstrated superadditivity of Persulphate with dichromate using the bleach compounded below:

Ammonium Dichromate	0.25 gm
Potassium Persulphate	20 gm
Potassium Hydrogen Sulphate	50 gm
Distilled Water	1 Litre

Superadditivity was noted by constituting the bleach with either the dichromate or the Persulphate missing. In each case the rate of bleaching dropped considerably. This important demonstration provides firm proof of the regeneration of dichromate ions in the  $\text{Cr}^{6+}$  form from the reduced  $\text{Cr}^{3+}$  form. Such bleaches are therefore capable of resolution improvement in dichromated layers by control of the lifetime of the  $\text{Cr}^{3+}$  ions. We also note that this type of bleach is capable of considerable variation of final metal ion content in the gelatin layer by control of pH. Subject to solubility constraints on the constituents, we can expect more metal ion content as the pH is raised.

We have also examined the role of the Kodak etch bleach EB2 compounded as follows:

Part A Copper Sulphate	120 gm
Potassium Bromide	7.5 gm
Citric Acid	150 gm
Distilled Water	500 ml

Part B 3% Hydrogen Peroxide solution

Distilled Water	500 ml
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N.B. The addition of Potassium Bromide effectively enables the Cupric Ion with its low Redox potential of 0.16 volts to attack the silver. Without the Bromide, the action will not proceed.

Equal parts are mixed just prior to use. The rôle of this bleach is traditionally to provide etched bars of gelatin in large scale (e.g. > a few  $\mu\text{m}$  in scale) lithographic images. Typically, such a bleach will destroy layers of high spatial frequency gratings and cause the developed zone to peel off into the processing solution.

**It is notable that the novel Ferric Nitrate-Persulphate bleach mentioned previously tends to exhibit a similar performance to the EB2 in terms of gelatin disruption when Peroxide is added, though it can still be disruptive in the absence of Peroxide.**

**(b) Acidified dichromate solution tends to increase the granular scatter of bleached silver halide layers.**

An often used technique to reduce printout in bleached silver-halide layers is to immerse the bleached layer in acidified dichromate solution. The reduction of printout sensitivity is dubious but a notable effect is an observed increase of grain in the bleached layer. Such ripening implies a detachment of silver halide from its protective colloid (the gelatin) which then permits a form of Ostwald growth.

**(c) If a Lippmann layer recorded in silver halide using a solvent bleach, is dried conventionally, it shrinks — moving its reflectance from the red of the HeNe for example, to a green colour. If it is dried in hot or graded Propanol, it emerges a red colour after drying.**

This effect is most striking and illustrates the power of Shankoff's method (Smith<sup>8</sup>) by which the bulk of the dried layer is recovered in the drying process. Obviously, such voiding as is generated by the removal of the silver is manifestly demonstrated when rapid drying in hot propanol is invoked. A case history is outlined in Figure 1.

Figure 1 — A two cell history of the solvent bleaching of a silver halide layer

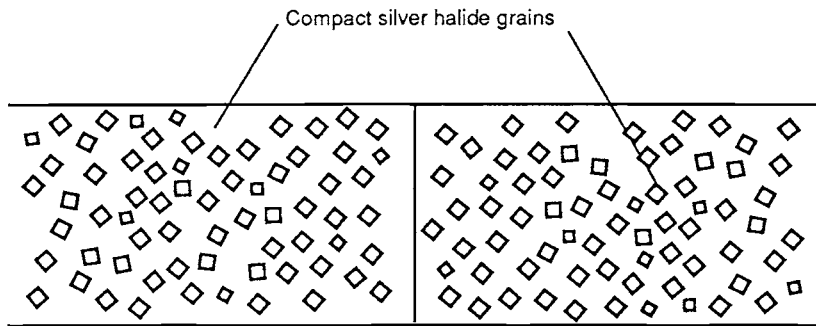


Figure 1.1 — Unexposed material

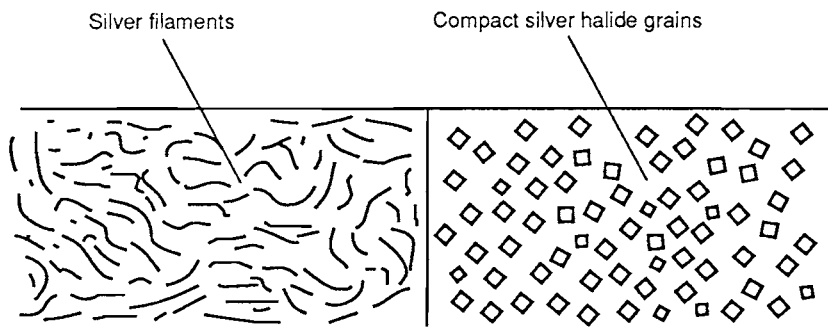


Figure 1.2 — Conditions after the development of the layer

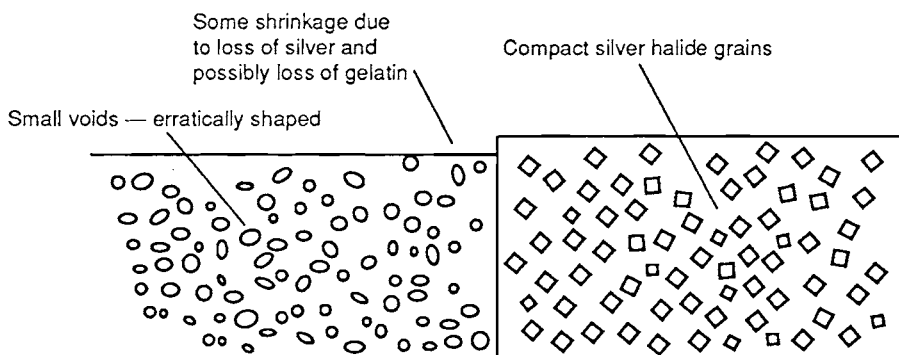


Figure 1.3 — Conditions after the removal of the silver filaments

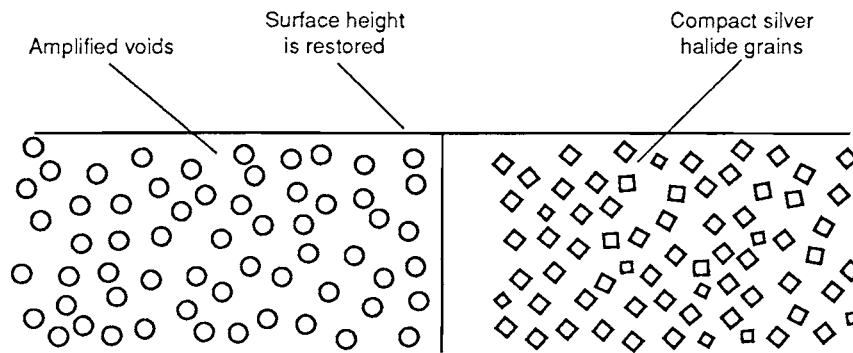


Figure 1.4 — Conditions after hot or graded propanol drying of the solvent bleached layer. Modulation is then determined by air voids and silver halide grains. Scatter can be high because the voids are shaped from the original developed silver filaments

(d) When D.C.G. layers are processed, then a gradual build-up of deposited gelatin is observed in the processing dishes or vessels. This observation has been confirmed by one of us (RR) over many years of work in the field of D.C.G. processing. One has to ask why does this situation arise — is it relevant to the underlying mechanism in the formation of the D.C.G. image?

(e) The bulk index of processed D.C.G. is in general less than in its preprocessed state.

This observation, again confirmed by one of us (RR), is the subject of much argument between various working groups. It seems extremely unlikely that the mean index of a D.C.G. layer can be in excess of its original unprocessed values. **Perhaps we could be more precise and say that the integrated optical path measured orthogonally to a gelatin layer is unlikely to increase as a result of D.C.G. recording and processing.** Our firm belief is that its always decreases.

(f) **If solvent bleaching of silver halide layers is conducted with ultrasonic agitation then the disruption of the gelatin layer is considerably greater than when the solvent action takes place without such agitation.**

**Ultrasonic agitation** has been found by us to be an effect way of clearing away the debris of gelatin hydrolysis which occurs when the bleach EB2 or our new bleach Ferric Nitrate (Sulphate) + Potassium Persulphate is used in an etch mode. In traditional crude etch bleaching, the gelatin surface is wiped over to remove the debris with, however, the risk of damage to the layer. Evidently, the loosening of gelatin present when etch bleaches are applied can be effected by either the deliberate addition of Hydrogen Peroxide to the bleach or the exploitation of some other aspect of the solvent bleach formulation to achieve the same end result.

### 3. A COLLATION OF IDEAS BASED ON THE OBSERVATIONS OF SECTION 2

In Section 2, we have observed a set of key phenomena which we believe give some clues as to the true fundamentals of the D.C.G. process. Let us consider a plausible train of events as depicted in Figure 2.

Figure 2 — A plausible two-cell history of dichromated gelatin

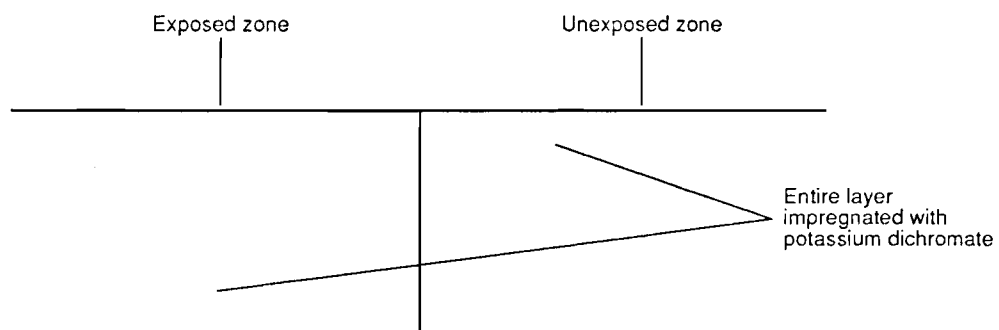


Figure 2.1 — Dichromated gelatin — initial conditions

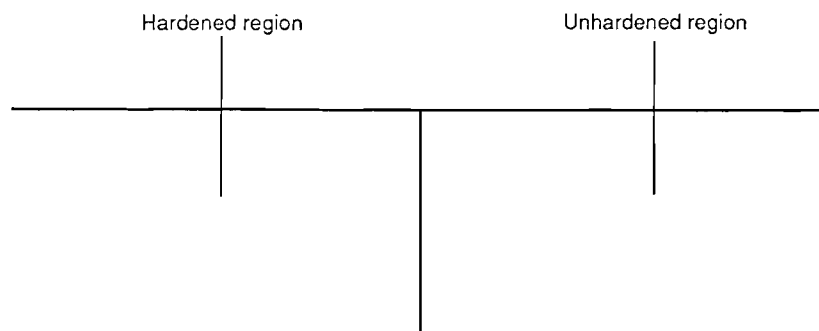


Figure 2.2 — Conditions after exposure to actinic light

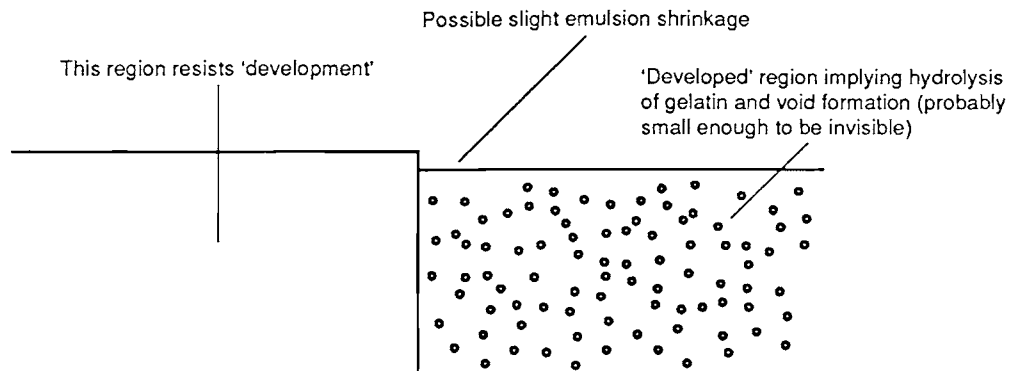


Figure 2.3 Conditions after 'development' — the hardening photographic fixer used increases bulk hardness of the unexposed zone and at the same time removes loosened gelatin. Modulation is amplified by void enlargement. Hardening fixers contain Chrome Alum hardener and a gelatin solvent — Acetic Acid.

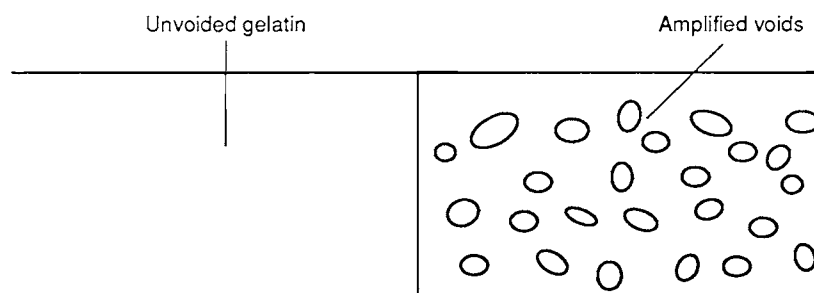


Figure 2.4 — Conditions after hot or graded iso-propanol drying in voids are now amplified, emulsion swells and layer thickness returns

- (i) The dichromated layer is exposed to the holographic light pattern.
- (ii) In the antinodal regions, a photo-induced hardening reaction takes place. **We shall clearly not argue against this long accepted and well proven idea.** However, we might suspect that dichromate in its unreduced form in fact softens gelatin.
- (iii) In the nodal regions some softening takes place together with a degree of gelatin hydrolysis which is controlled by 'development' in a hardening fixer. Here 'development' describes a process involving some hardening of the layer and we should remember that some hydrolysis may be encouraged by certain constituents of the fixer.
- (iv) Shankoff's rapid or graded drying process allows the regions of partially hydrolysed gelatin to expand so as to contain amplified air voids.

In sub-section (iii) we see an essential and simplistic ingredient in which the unusually large levels of index modulation are easily explained.

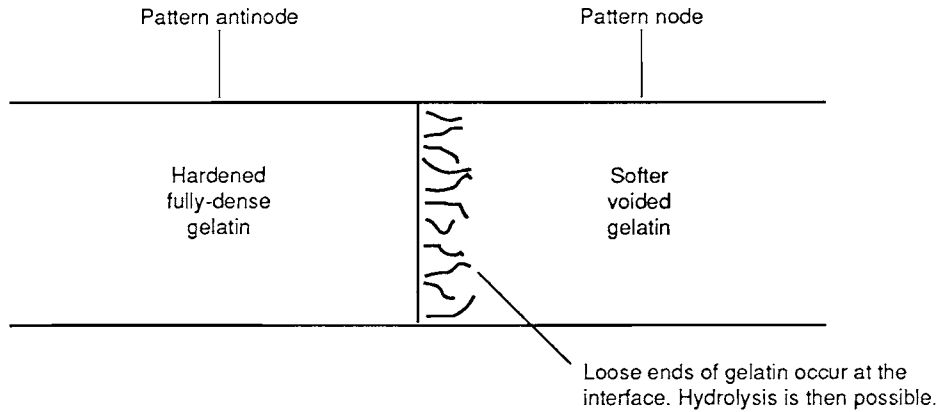
Clearly, the photo hardening reaction is very important in providing resistance to hydrolysis. **The hydrolysis itself and its origins will be discussed in detail in the next section.**

#### 4. REASONS FOR THE HYDROLYSIS OF GELATIN

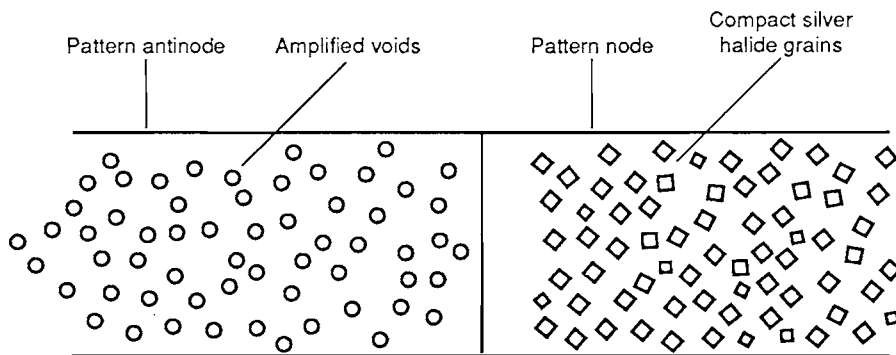
If we consider the action of the bleach EB2 then we can see that hydrogen peroxide is added to provoke hydrolysis of the gelatin. It does this by acting on the loose ends of gelatin created when the silver removal breaks the protective colloidal structure of gelatin thus liberating free ends of the protein structures. These loose ended structures are made hydrophylic by the attachment of functional groups which originate from the peroxide in solution. Many other gelatin solvents exist, the most pertinent being Acetic Acid commonly used in fixer buffers.

When gelatin is photo-hardened then neighbouring zones will have loose ends available as can be seen from a binary two zone model shown in Figure 3.

**Figure 3 — A comparison of the two chosen models showing the basic difference between D.C.G. and the solventbleached silver halide**



*Figure 3.1 — A simplistic view of the final D.C.G. image.  
Note that the higher index material is located at the antinode of the pattern*



*Figure 3.2 — The final result for a solvent bleach silver halide layer dried in hot or graded Iso-propanol.  
The highest bulk index coincides with the pattern node*

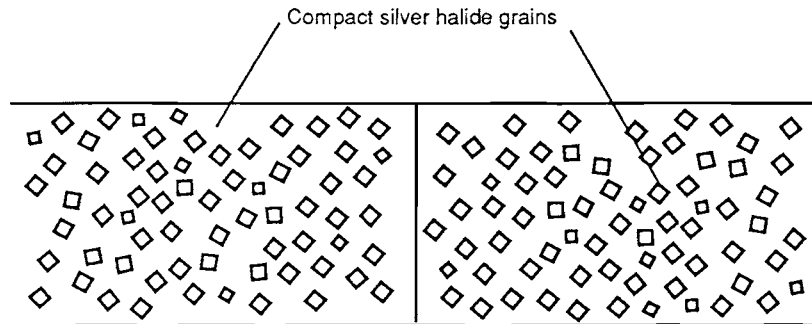
On the right hand side of the interface then loose ends from strands of gelatin in region 2 cannot be tied up in the hardening reaction present in region 1. Under such conditions, the ends at the boundary of region 2 can be caused to have an affinity to water (hydrolysis by the action of  $H_2O_2$ ). The problem is a little like the Van der Waals forces at the surface of a gas or liquid — an essential anisotropy is introduced.

We note that the observed granulation of silver halide layers mentioned in Section 2(b) is explainable by a degree of hydrolysis caused by an interaction between the gelatin and the bleach solution. It seems likely that any solution containing agents of high enough redox potential is capable of a similar effect. We might expect the hydrolysis of gelatin (as the attached protective colloid of the silver halide layer) to be triggered off by the presence of any suitable agent such as  $H_2O_2$  which can create hydrophylic conditions for loose gelatin strands. In the case of the silver halides, the necessary loosening is created by the solvation of silver grains.

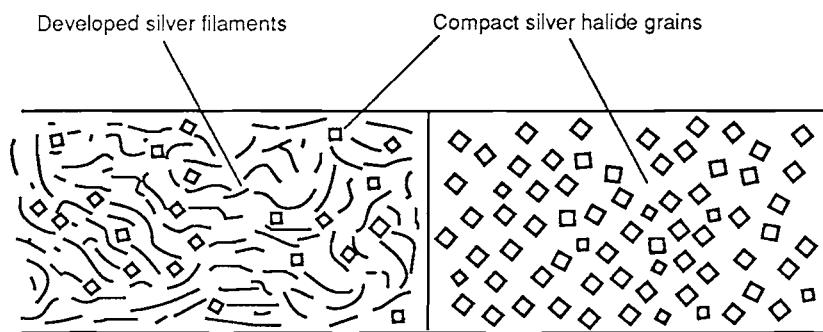
### 5. AN ALTERNATIVE STRATEGY FOR THE CREATION OF S.H.S.G. BY REVERSAL PROCESSING

This method was introduced in the belief that previous studies were somewhat restrictive and to an extent flawed since they failed to provide adequate spatial frequency response of the recording. The inherent difference of this new method lies with avoidance of the use of fixer or excessively rapid solvent bleaches. Such questionable solvent bleaches include Permanganate. The method, though a trifle tedious, allows another look at the removal of silver and its halides in an extended step by step procedure.

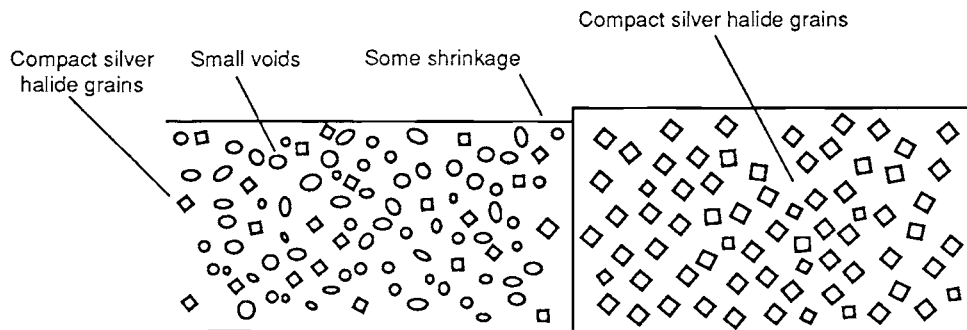
*Figure 4 — A case history of the formation of voided or phase modulated gelatin (S.H.S.G.)  
— a new chemical approach*



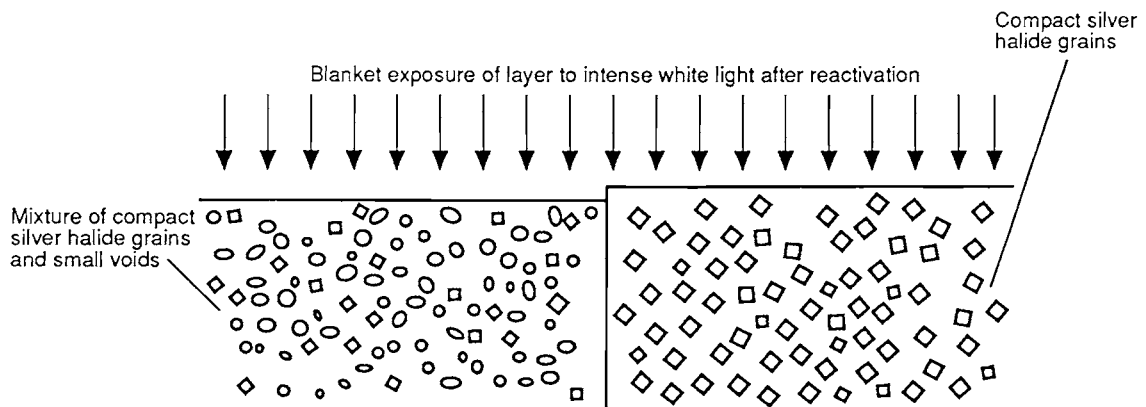
*Figure 4.1 — Initial state of two cell layer*



*Figure 4.2 — Showing partial development of the left hand cell and consequent creation of silver filaments*



*Figure 4.3 — The left hand cell has now lost its silver by the action of a solvent bleach*



*Figure 4.4 — Intense white blanket exposure is used to make all the reactivated grains developable*



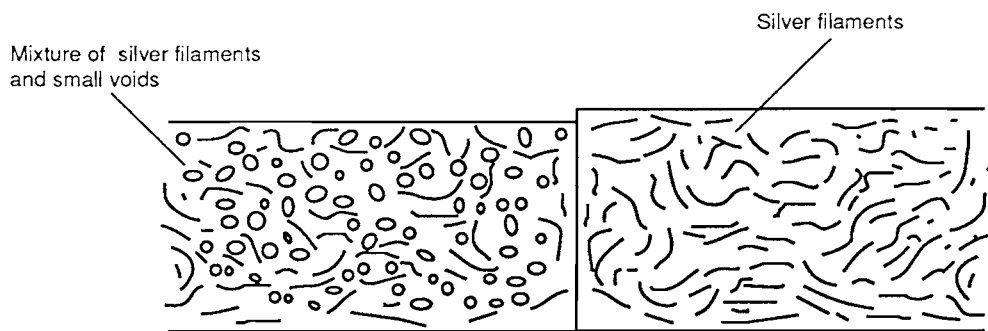


Figure 4.5 — The structure now contains only silver filaments and voids (in the left hand cell) after second development

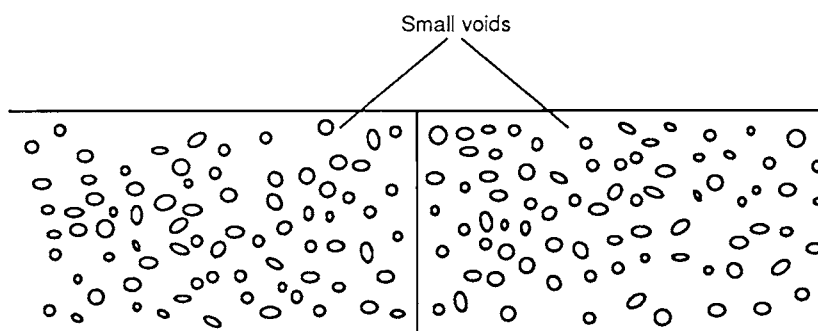


Figure 4.6 — Further application of the solvent bleach leaves small voids in both cells

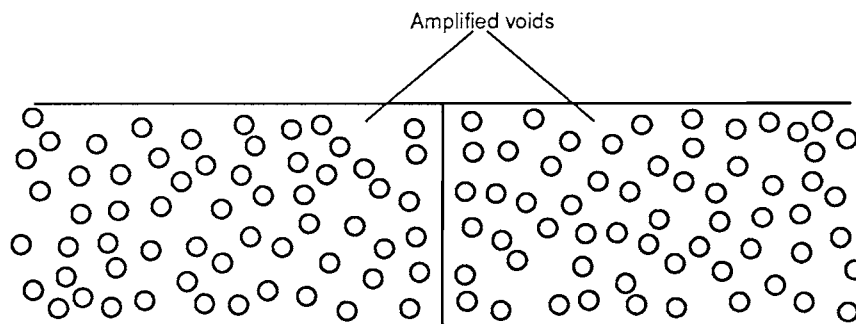


Figure 4.7 — Voids are now amplified using hot or graded Propanol drying

## 6. DISCUSSION

Dichromated gelatin offers a uniquely interesting set of attributes both in its capabilities for high index modulation and in the simplicity of processing. Possibly, the substitution of the dichromate family by other chemical compounds is inhibited by the need for those other compounds to have a similarly potent photo-hardening or reduction hardening reaction. For example, the ferric compounds (Nitrate or Sulphate) being brown certainly have a reasonable ability to absorb actinic light or even mid-spectrum green. The general wisdom however is that their photo-hardening ability, though significant, is not the same as that of the dichromate family.

The reader is referred to the book by Kosar<sup>9</sup> (page 39) for a discussion of the role of Ferric and Ferrous compounds on the cross-linking of gelatin. Evidently, the **Ferric** ion can assist gelation of a gelatin solution though the ion is converted to Ferrous by the action of actinic light. **Ferrous** ion causes gelatin to soften making it prone to hydrolysis.

This situation allows some fascinating processes such as the True-to-Scale Process in which Ferricyanide from a blue print transfers by contact into a moist gel containing Ferrous ion. The oxidation of the Ferrous ion to Ferric by the ferricyanide then insolubilises the gelatin in that region of contact. Interestingly, the Ferric bleach mentioned by us in this paper contains a regeneration mechanism for the Ferric ion. As the Ferric ion is reduced by oxidation of local silver then the Potassium Persulphate can

regenerate the original Ferric population from the Ferrous population. It is our belief that further studies of the relative proportions of Ferric (Nitrate/Sulphate) and Potassium Persulphate will reveal new methods of manipulation for the silver halide layers discussed earlier. We note however, that photo reaction and bleaching reaction will only create softening Ferrous ions.

The softening of gelatin by Ferrous ion reveals some interesting properties of the solvent bleach process discussed in this paper. As the silver is removed thus leaving voids in the layer then the gelatin is simultaneously softened by the generation of Ferrous ions. Softening and silver removal are of course synergistic processes.

The overall integrity of the gelatin thus suffers and indeed, the recorded region of silver halide may just peel off the substrate after bleaching especially if ultrasonic agitation is invoked. In the case of the dichromate bleach, the synergism is violated since silver removal is accompanied by local hardening of the gelatin.

Now we can reconsider an alternative solvent bleach namely acidified dichromate solution. Does such a silver solvent bleach tan the gelatin layer or does it soften it? Clearly, reduced dichromate ( $\text{Cr}^{3+}$  ions) harden the layer but dichromate itself can palpably effect some gelatin softening.

The work related in this paper is of course derived in the main from studies of silver halide layers in which development is followed by removal of silver or its re-halogenation.

We found that non-tanning developers such as Ascorbic Acid left the layers prone to attack by hydrolysis and hence risked detachment of the gelatin layer during solvent bleaching. Since the tanning developers such as Catechol create oxidation products that tan, it is assumed that the nodal regions are tanned by diffusion of these products from the antinodal region. Re-halogenating bleaches delay salts removal until the fixer stage and thus provide greater integrity of the layer.

The interesting difference of integrity of layers which were ultrasonically agitated during bleaching and those that were free from agitation provided strong insights into the presence of gelatin hydrolysis in the weakening of the recorded layer.

Some of the reporting of bulk index changes in D.C.G. layers have a degree of unreliability. Obviously, the bulk or average index of a gelatin layer can only decrease bearing in mind the effect of hydrolysis and could only increase if serious physical compression was invoked or if metal ion addition ( $\text{Cr}^{3+}$ ) is considered.

The observation 2(c) of recovery of layer thickness during hot isopropanol drying is most interesting because it implies a sort of 'memory' built in to the gelatin layer that pre-disposes it to return, when forced, back to its original thickness before recording. Of course such an observation is not precise and is probably capable of serious modification if required but its simplistic description provides a working start point.

## 7. A REFINEMENT OF THE PROCESS FOR THE CREATION OF SILVER HALIDE-SENSITIZED GELATIN (S.H.S.G.)

In refining the technique for the creation of S.H.S.G., we have collated the phenomena described in the text.

As Chang and Winick<sup>4</sup> have pointed out, the highest levels of modulation with this process occur when bleaching involves re-halogenating of the silver image. Extremely careful optimisation of the whole process has been undertaken by Fimia *et al*<sup>10</sup> and we refer the reader to their work.

**We can see from the arguments of this paper that since the silver is not removed from the developed site when re-halogenation of the silver takes place then the formation of hardened shells around the bleached silver site is enhanced by non-removal of the contents of each shell. The removal of silver halide by the subsequent fixation stage then gives the shell a chance to harden before its contents are removed to form a void.**

We believe that the arguments given concerning the superiority of re-halogenation over silver solvation in the bleach phase purely relate to this synergism of hardening with non-removal of the silver (dichromate) and softening with removal of the silver (Ferric).

Arguments about control of lifetime of the  $\text{Cr}^{3+}$  ion by the presence of KBr are weak since the lifetime of  $\text{Cr}^{3+}$  can only be directly controlled by a regeneration agent such as Persulphate which provides a re-oxidation capability.

In our revised process procedure for S.H.S.G., we have adopted the procedure shown at the end of the paper in the Chemical Formulary section.

## 8. A BRIEF SEARCH FOR ORGANIC HARDENING BLEACHES

We undertook a search for an organic substitute for the dichromate usually used in hardening bleaches. A basic problem of symmetry emerges; developing agents can liberate hardening oxidation products as the image is developed but bleaches of the organic type (e.g. Quinone) simply create the reduced form of the oxidant (Quinol in the case of Quinone). Thus the liberation of a hardening product such as the  $\text{Cr}^{3+}$  ions of the dichromate bleach is not present in simplistic chemistries. We examined all of the organic bleaches mentioned in our paper<sup>7</sup> cited here but without success. It is truly strange that we cannot simply replace the dichromate  $\text{Cr}^{3+}$  ion in an easy way.

## 9. CONCLUSIONS

This paper makes a comment on the technology of D.C.G. and S.H.S.G. The complex and often tortuous discussions of where the modulation levels come from are easily focussed if gelatin hydrolysis is invoked. The set of observations presented here provide a talking point for new investigations and offer a degree of the 'heresy' suggested by the title namely that dichromate can both tan (or cross-link) gelatin and at the same time effect its hydrolysis.

It is probably true to say that the S.H.S.G. process relies on the integrity of complex oxidation product deposits in the gelatin — liberated at both the develop and bleach stages. This paper has discussed the convoluted arguments that relate to the role of the interaction of metal ions with photographic gelatin. Hardening or softening can be induced. However, such bleaches as described in this paper have to be tailored cleverly to provide the greatest interactive capability of the particular metal ion species with the material in use. Generally, as the pH is increased, an observable increase of ionic interaction can be noted from the increase of colour of the bleached layer. Such considerations are of course limited by the availability of suitable ionic compounds and appropriate buffers. As we pointed out in the text, the Ferric bleaches mentioned here are not correctly pH balanced.

In conclusion, we can see that chemically induced reduction of oxidising metal ions can simulate the photo-induced effects of the D.C.G. process. With some care, the S.H.S.G. process could well become more popular if the high speed development process mentioned here is invoked. The bottom line is the solution to the problem of the hydrophylic nature of the final end product. To date, this has only been partially successful and will now merit a major attack to close it off finally.

## 10. ACKNOWLEDGMENTS

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### CHEMICAL FORMULARY

#### Silver solvent bleaches

SS1. Ferric Nitrate (Sulphate)	100 gms
Potassium Persulphate	20 gms
Distilled water to 1 Litre	

H<sub>2</sub>O<sub>2</sub> can be added for etching purposes.

*This bleach is a softening regenerative bleach used by us for reversal processing of lithographic images, especially when etching of high resolution images is required (with the addition of H<sub>2</sub>O<sub>2</sub>).*

SS2. Ammonium Dichromate	10 gms
Potassium Persulphate	20 gms
Potassium or Sodium Hydrogen Sulphate	2 gms
Distilled water to 1 Litre	

*This bleach is compounded to provide enhanced concentration of Cr<sup>3+</sup> ions for hardening of gelatin with control of resolution and regeneration by the Persulphate. It cannot accept H<sub>2</sub>O<sub>2</sub> for hydrolysis of gelatin.*

*N.B. In these bleaches regeneration of the reduced silver oxidant is effected by the Persulphate which itself cannot effectively attack silver because of a double layer problem. This helps the confinement of the reduced oxidant to sites close to the silver site that is under attack. For re-halogenation, both bleaches were augmented by 20 gm of KBr.*

#### 3. Eastman Kodak's etch bleach EB2

*This bleach produces major gelatin hydrolysis. It is often preceded by hardening fixation or a chrome alum bath to avoid major disruption of the gelatin layer.*

Part A Cupric Sulphate	120 gms
Potassium Bromide	7.5 gms
Citric Acid	150 gms
Distilled water to 500 ml	

Part B Hydrogen Peroxide 3%	500 ml
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*Mix equal parts just before use.*

*N.B. Bleach SS1 will etch in just the same way as EB2 by the addition of Hydrogen Peroxide.*

#### Developer for silver halide-sensitized gelatin (S.H.S.G.)

*The Eastman-Kodak concentrated developer HC 110 is a simplistic developer for S.H.S.G. but workers with access to the Agfa lithographic concentrates should see the advice below.*

### Reactivator solution RA

Sodium Sulphite (Anhydrous)	50 gms
Sodium Hexametophosphate	1 gm
Distilled water to 1 Litre	

### A modified method for the production of S.H.S.G. — a reversal process

1. Develop in HC 110 developer diluted to 1 + 30 to 1 + 60 at 20°C or preferably in Agfa's G284c concentrate (see note below).
2. Wash 5 minutes.
3. Solvent bleach in SS2: Agitate scrupulously and carefully — an insoluble precipitate is formed in the bath and may bond to the hologram surface if care is not taken. We might recommend recirculation of the bleach with particle filtration included. Allow time for all developer stain to clear.
4. Wash 5 minutes.
5. Reactivate in solution RA — 2 minutes.
6. Wash 2 minutes.
7. Expose to an intense white light.
8. Develop to completion in HC 110 or any suitable high energy developer.
9. Wash 5 minutes.
10. Solvent bleach in SS1. Wait until all stain is cleared. For agitation instructions, see above.
11. Wash scrupulously and use hot or graded Propanol dehydration.

### A refined process for the production of S.H.S.G. using high speed development and regenerative bleaching

1. Develop in Agfa's lithographic concentrate G284c (the first developer for high speed reversal processing of Agfa's Millimask product). Here, remarkable emulsion sensitivities have been observed — for Agfa materials, better than 30  $\mu\text{J}/\text{cm}^2$  in the red and green spectra and with considerable improvement in the far blue at 457.9 nm. We were surprised by the low fog levels accompanying this speed advantage — normally, we might expect to require 300  $\mu\text{J}/\text{cm}^2$  in the red and green spectra. The availability of G284c is under question. The vast stocks we have available may have outlasted availability — workers should enquire what the current part number is in relation to the Agfa reversal process for Millimask.
2. Wash.
3. Re-halogenate in the bleach we shall call S.R.H. 2:

Ammonium Dichromate	10 gm
Potassium Persulphate	20 gm
Sodium Hydrogen Sulphate	2 gm
Potassium Bromide	20 gm
Distilled Water	1 Litre
4. Wash.
5. Fix 5 mins. in hardening fixer.
6. Wash.
7. Soak in warm water (c 30°C).
8. Immerse in 50 : 50 Propanol–Water at 30°C.
9. Immerse in 100% dry Propanol at 30°C.
10. Dry under a bank of infra-red Tungsten Halogen lamps.

### Authors' Note

**NB** Since the inception of this work, we have found advantage in the use of the Agfa developer G284c in Stage 1 which is compounded for **lithography**. Such developers usually contain halide solvents and encourage sharp developed edges to form in the recording. Such behaviour actually endows the emulsion with a notable speed gain when compared to normal high contrast development (say in HC110). Thus we have been able to observe sensitivity of the order of  $10 \mu\text{J}/\text{cm}^2$  at 488 nm with Ilford's special Blue/Green sensitive holographic material i.e. some three orders of magnitude better than D.C.G. itself. This emulsion is unfortunately now discontinued but a good substitute is Agfa's Millimask HD mask making material for which G284c was specially compounded. Specialised developers such as this tend to increase the level of fog which is deliberately restrained in Millimask. Agfa's Holotest materials can also be used but will exhibit higher fog levels than Millimask. We have also tested Kodak products such as Maximum Resolution Plate 1A with good results. Fog level with G284c has not been a problem however.