The Silver Halides – the Workhorse of the

Holography Business

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Abstract

The purpose of this paper is to provide an update on the status and use of the silver halides in the formation of holographic images. The writer's review of the subject (S.P.I.E. Vol. 532, Los Angeles 1985) is updated to include certain important areas of improved understanding particularly in relation to rehalogenating bleaches. Some important recipes are included which give reliable results in the absence of toxic hazards. A new possibility is proposed in which post processing swellants recover the thickness of the gelatin in a permanent fashion.

1. Introduction.

Since the rapid expansion of the technology of holography in the early 1960s, the silver halide materials have occupied a prominent place in the recording of images. The reason is primarily the high sensitivity of the recording medium thus permitting the use of minimal levels of sensitizing light and hence easing the stability problems of apparatus and the need for high powered laser equipment.

From the very beginning of this important phase of work, it has been accepted that the silver halides are of an inferior character to say the grainless media such as dichromated gelatin or the photopolymeric materials. This opinion is based on the problems created by the scattering properties of photographic grains and the observed fact that badly processed silver halide layers often exhibit an unhelpful level of scatter, thus preventing the use of the medium in areas such as optical element fabrication for example.

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As the technology has advanced, then workers have seen gradual improvements of diffraction efficiency to the point at which few complaints can be made since both high efficiency of diffraction and good agreement with theory have been observed. It is interesting however to review the situation at this stage since there is a lack of unification of approach to the use of the silver halides that has been brought about by the radical difference of approach to their use in Soviet and 'Western' laboratories.

In this paper we shall look at some of the properties of silver halide layers suitable for holographic recording and pay special attention to methods of processing subsequent to exposure. It will become clear that there are many ways of forming a holographic image, but in fact very few that create an accurate image in terms of the geometry of the interference planes created in the layers.

We shall pay attention to the use of bleached and unbleached holograms and attempt to understand the fundamental differences inherent in the use of 'black' silver development followed by some form of bleaching and the Soviet 'colloidal' approach to the problem using 'brown' silver.

Recent work has again highlighted the need for a better understanding of the problems of reciprocity failure during the sensitization of the layer. We shall look at the problem of point by point recording of images and its dependence on advances in this area of work.

In a field such as this, it has been felt wise to concentrate on a few key papers which outline highly individual areas of attack on the image-forming problem. This approach inevitably means that some important papers will be overlooked. Such is the rather confused state of affairs (internationally) however that it was thought wise to approach the arguments with an attempt to unify the overall discussion and the disparate practical and theoretical approaches.

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2.   Parameters of Unexposed Silver Halide Bearing Layers Suitable for Holographic Recording.

The characteristics of photographic layers suitable for holographic recording have now been well defined by dint of considerable experimentation worldwide. Early theoretical discussions suggesting that layers of gelatin of thickness 15μm or more would be needed for serious approaches to volume holography have now been largely swept aside by practical reality. Indeed, there is a current acceptance both in the west and in the Soviet Union that layer thicknesses of more than 10μm are neither of practical use nor of theoretical importance except in extreme cases.   In an important paper Hariharan (1) has pointed out that in Lippmann holography then as the layer thickness increases, the wavelength selectivity of the hologram also increases. The implicit result is that the perceived luminance of Lippmann holograms must diminish if the layer is made too thick because the bandwidth of the reflected light drops away. Of course, this presupposes that one can effectively process such 'thick' layers anyway and considerable Soviet effort in this area has left the impression of very considerable difficulties vis-a-vis processing of layers of thickness greater than 10μm.

The structure of a typical holographic silver halide bearing layer is by western standards as follows:

Typical Plate   Typical Film
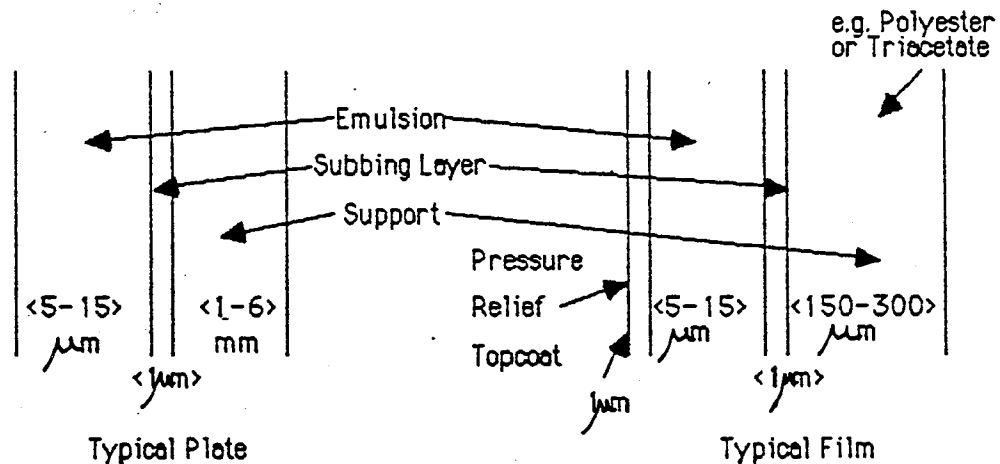
The plate structure has a typical glass support usually 1 – 6 mm thick, onto which is coated an adhesive or 'subbing' layer. The silver

halide bearing gelatin is then coated onto the subbing layer. In a film product the emulsion surface is usually coated with a 'pressure relief' layer which avoids the appearance of pressure marks on the film after development. This layer is absolutely vital in the x-ray film business for example and its absence may lead to false diagnosis of some defect in a patient. In the holographic context, the layer may cause problems in that in certain Lippmann work it forces the sensitive zone of the emulsion away from a contact reflector for example.

The question of grain size is of considerable importance but the practicalities of coating the emulsion probably influence the results obtained more than the achievement of a **low** nominal grain size. An examination of the scattering of light created by the grains (in the Rayleigh limit) shows that a parameter ξ denoting the ratio of the scatter mean free path to the emulsion thickness can be used as a figure of merit to describe the layer in question. This parameter is presented in a recent paper by Phillips et al (2) and is calculated to be:

$$\xi = 1/N\sigma_{RS}d$$

where N is the number of grains/unit volume of the emulsion, d is the emulsion thickness and σ_{RS} the Rayleigh scatter cross-section given by:

$$\sigma_{RS} = \frac{\pi}{12}\left[\frac{2\pi}{\lambda_a}\right]^4 \frac{n_G^4(n_H^2 - n_G^2)^2}{(n_H^2 + 2n_G^2)^2}\Lambda^6$$

Here λ_a is the wavelength of light in air, n_G and n_H are the respective refractive indices of the gelatin host and the halide grain, and Λ is the grain diameter.

We note that when $n_H \rightarrow n_G$ then σ vanishes and the grains are not discernible as we must expect. Relation of N to the coating weight of the emulsion permits the calculation of a numerical value for ξ for a specific case. One arrives at values $\xi = 5$ for Agfa's 8E75HD and $\xi = 0.6$ for 10E75. We conclude from this that the fine grain (low speed) 8E75HD material is just about good enough for serious work whereas the 10E75 material poses

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problems (certainly in the Lippmann case).

Such numerical estimates are arrived at by utilising a mean grain diameter figure of 0.044μ for 8E75HD and 0.09μ for 10E75.

Mean grain size figures of the order of 0.035μ are quoted as relevant to Agfa's 8E75HD and are typical of the average 'western' materials used by the bulk of scientists outside the Soviet Bloc countries. There is certainly some lack of agreement between Agfa's precoating grain size estimate and the size as measured from the coated layer. This is fairly typical of the problem of large-scale coating of such exotic materials. The risk of grain growth between preparation of the emulsion and coating is always present. More importantly, the presence of 'mistakes' in the tail of the Gaussian grain size distribution can totally upset the properties of the emulsion in the scattering context. The perceived turbidity of the layer may thus be dominated by relatively few large grains in the Gaussian (or non-Gaussian) tail. This problem has been given special attention in new Ilford emulsions which have been designed for very low turbidity coupled with high photographic speed (grain size c. $0.04\mu m$).

Soviet and Bulgarian emulsions have typical grain sizes of the order of $0.01\mu m$ to $0.02\mu m$ and thus offer considerable scatter advantages over the western product. Such true Lippmann emulsions appear totally clear and glassy prior to exposure.

It is probably true that the range of grain size suitable for serious holographic work is something like $0.01 - 0.035\mu m$. Grains whose sizes are above the maximum exhibit excessive scatter and those whose sizes are less than the minimum exhibit virtually no usable sensitivity. Of course 'sensitivity' must be seen in the context of what 'grainless' media have to be exposed to. We are probably expecting a holographic silver halide emulsion to have a sensitivity of the order of $1 - 300$ $\mu J/cm^2$ to achieve a developed density of usable proportions (D = 2 - 3). If we have to give another one to two orders of magnitude exposure, then we begin to object and we naturally gravitate to dichromated gelatin or the photopolymers.

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There clearly is a rôle for ultra-fine grain developable media which require exposures intermediate between the extremes set by the halides and the 'grainless' media.

The characteristics of the gelatin host are important in permitting appropriate diffusion transfer mechanisms to take place. Thus at one time it was thought that the gelatin should be as hard as possible to prevent shrinkage effects during processing. That such shrinkage is sometimes inevitable is now obvious. However, if salts are removed from overhardened layers then the net result is usually the formation of voids which act as scattering centres in just the same way as do the grains of the silver halide media. It is a fact that the Kodak materials are on the overhardened side of the working limits and that recent Agfa products have been steered in the same direction. We shall see later on that diffusion transfer during processing is an important process in the manipulation of the silver hailide material. When the gelatin is too hard then the resultant inhibition leads to a reduction of image modulation and low efficiency in many circumstances. The trend towards overhardness has thus been moderated in the new Ilford product and the aim will be to offer usable hardness coupled with the ability to exhibit good diffusion transfer characteristics. Hardness should not be confused with adhesion of the gelatin layer to the substrate. In the past, there has been a confused view of the rôle of hardness and 'softness' has often been blamed for lack of emulsion adhesion during processing.

3. Methods of Image Modulation – Development and Bleaching.

Various important methods for forming the image exist and in this section a selection of important and well-delineated papers will be discussed.

a) Amplitude holograms – the production of the silver image.

The production of amplitude holograms is thought of as being extremely simplistic. Virtually any high contrast developer will yield usable results and inevitably the use of conventional development schemes leads to the formation of filaments or worms of **black** silver.

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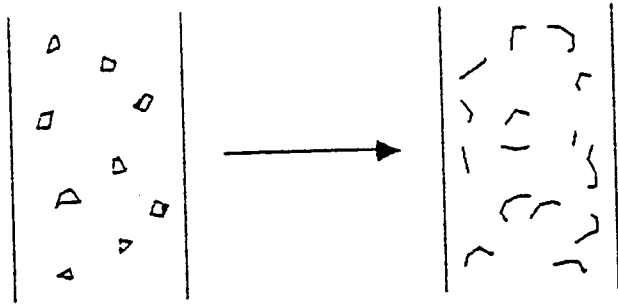
Compact Grains of Halide become Worms or Filaments
of Silver in Normal Developement

Conventional developers convert compact grains of silver halide to worms or filaments of black silver. If the developed image remains **unfixed** then the efficiency of the hologram has both amplitude and phase contributions and the efficiency can rise above the typical few percent of the plain silver image hologram.

Filaments are endemic to the normal development process and are always associated with the latter stages of development. The early stages may, however, exhibit the formation of small spherical lumps of silver depending on the nature of the developing agents used. A discussion of the subtleties of the compact growth to filamentary growth transition is given for example in James (3).
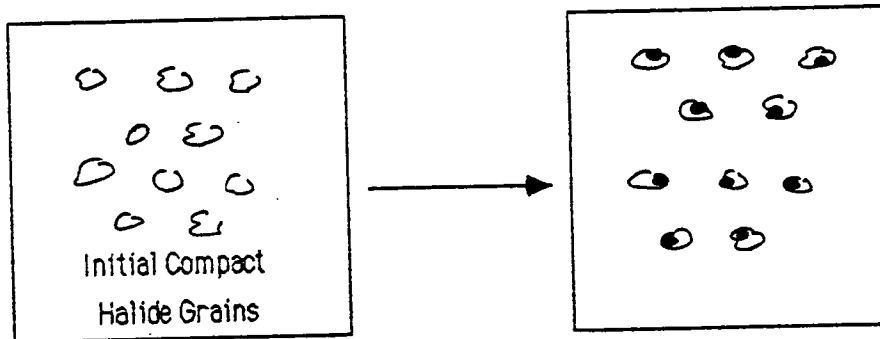
Typical Early Metol-Ascorbic Grain Development

Early stages of development may involve compact silver growth in small spheres.

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The inevitably of filamentary growth and the **black** appearance of the silver can be overridden however by the introduction of high levels of restrainer (e.g. bromide) to the developer and typically early photographers used to lace their developers up with high bromide levels to create what they called 'warm' tones. What they were in fact doing was to alter the morphology of the silver and thus create spherical particles at least in part. Such spherically structured silver is loosely known as colloidal when the particle diameters lie in a range of the order of 0.01 - 0.05 μm. The colour of the silver so produced tends to be reddish-brown and the particle diameters decrease with increasing exposure.

Such early photographic work thus predated much of the invention of the latter day Soviet colloidal holography by some eighty to ninety years. It was of course inevitable that with such levels of restraint, then the overall exposure of the media had to be increased often by some four to five times.

Colloidal silver development forms the basis of most of the modern Soviet work and the reader is referred to the aricle by Denisyuk (4) for a suitable bibliography of the immense Soviet effort in the field. However, a recent paper by Zhang and Zhang (5) presents some very neat and beautifully-presented results of a careful study of the colloidal image in relation to diffraction efficiency. Their article is based upon the theoretical analysis of a medium consisting of colloidal particles capable of creating both amplitude and phase modulation simultaneously. Such a medium is shown to be elegantly described by the theory of Maxwell-Garnett (6) dating from the year 1904.

Colloidal development permits the formation of holographic images using only a developing stage. The specific visual opacity of **brown** silver is lower than that of **black** silver and thus fairly high levels of efficiency ($\approx$ 50%) can be achieved without any further stage of processing.

Obviously, holograms that absorb light cannot yield efficiencies near the 100% mark, but the light scattering properties are extremely advantageous and the efficiency is often accompanied by very low levels of background noise.

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The bulk of Soviet reflection holograms are created by the technique of colloidal development using true Lippmann emulsions with grains of the order of 0.01μm to 0.025μm in size. In fact, the colloidal development scheme is almost imperative in their case since such ultra-fine grain emulsions do not process in the same way as emulsions with grain sizes of around 0.04μm.

For the interest of readers, we revisit the formulation of the ubiquitous Soviet colloidal developer GP8. The formulation is unusual in normal terms in that a high level of halide solvent (Ammonium Thiocyanate) is present. It is this agent that helps to create the required conditions for the production of a colloid. The development is best performed in de-ionized water due to the dilution of the solution and is fussy in that it may throw up dichroic fog and silver on the surface of the emulsion.

GP8 Developer (Soviet Colloidal)

Phenidone	0.026 gm
Hydroquinone	0.65 gm
Anhydrous Sodium Sulphite	13.00 gm
Potassium Hydroxide	1.38 gm
Ammonium Thiocyanate	3.12 gm
Distilled water	1 Litre

Develop for 6 minutes at 20 ^{o}C

Many Soviet formulations now exist and indeed one of them, P.R.G.1, replaces the Ammonium Thiocyanate with a very high level of Potassium Bromide:

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┌──────────────────────────────────────────────────────────────┐
│                                                                │
│         P.R.G.Developer          (Soviet Colloidal)            │
│                                                                │
│    Part A                          Part B                      │
│    Anhydrous Sodium Sulphite 38 gm  Potassium Hydroxide 240 gm │
│    Hydroquinone              30 gm  Distilled Water    1 Litre  │
│    Potassium Bromide         22 gm                             │
│    Distilled Water           1 Litre                          │
│                                                                │
│                                                                │
│    Mix one part A with one part B and 13 parts distilled water.│
│    Develop for 25-30 minutes for Lippmann emulsions.           │
│                                                                │
└──────────────────────────────────────────────────────────────┘
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Here we see history repeating itself, albeit with somewhat more than an alchemistic view of the underlying mechanisms: (The Soviet work is backed up by the most exacting electron microscopy of grain structure).

In concluding section a), we note that the colloidal development is capable of a very close approach to theoretical ideals. The small spheres of silver and the residual halide make for an almost perfectly predictable system. By contrast, the black silver methods are relatively crude and involve considerably greater amplification factors than the colloidal process.

b) Development (black silver) followed by silver solvent action – reversal bleaching.

Exposed Zone   Developed Zone   'Bleached' Zone
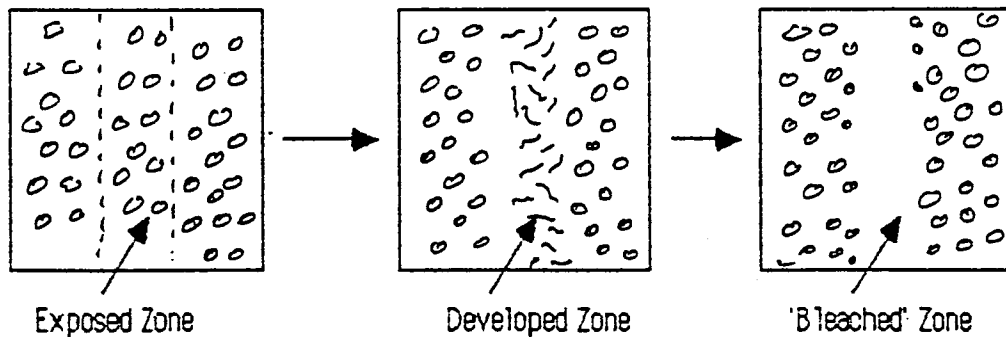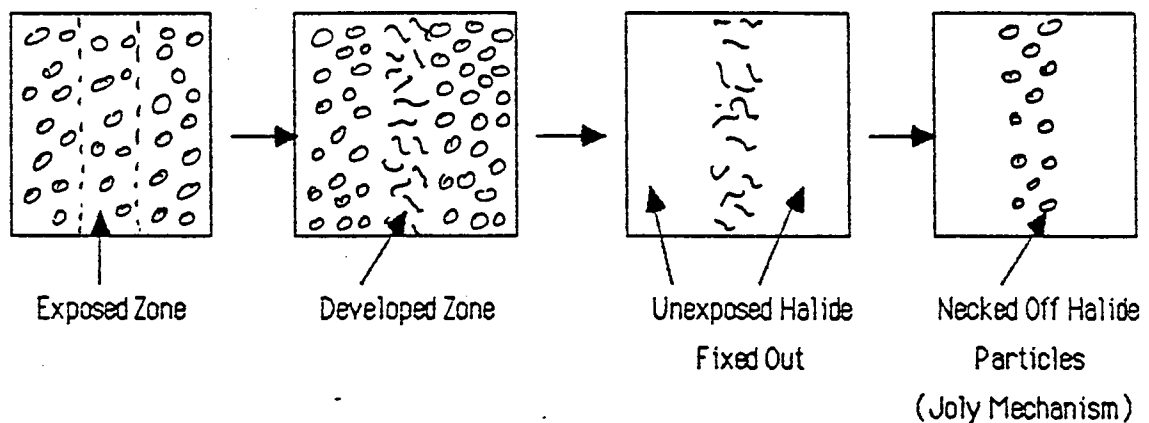
This technique is of great interest historically since it formed the

basis for the early Agfa-Gevaert process procedure and many workers will have cut their teeth using this technique. The advantages stem from the fact that silver solvents are invariably tanning in action, e.g.: Potassium Permanganate; Potassium Dichromate; Ammonium Dichromate; Pyridinium Dichromate; Ferric Nitrate.

Acidified solutions of the above agents act to ionize the silver and then complex it away into the processing solution. Due to the tanning action, it is easy to create voids in the layer as the silver is removed and thus to create problems of enhanced scatter in the layer. Van Renesse's (7) 'Pyrochrome' process in fact recommends the production of reflection holograms using the agent Pyrogallol followed by silver solvent action to 'bleach' the resultant image. With a few tricks added, this basic process makes good quality reflection images in an extremely simplistic way. Nonetheless, the removal of salts is not helpful to the achievement of the highest reflection efficiencies in Lippmann layers, as we shall see later.

As a simplistic method with clean results free from surface relief effects in the layer, the reversal bleach process has few rivals however.

c) Development followed by fixing and rehalogenation.

Exposed Zone   Developed Zone   Unexposed Halide   Necked Off Halide
                                    Fixed Out   Particles
                                                         (Joly Mechanism)

This technique has achieved great popularity and when properly applied is capable of creating results of very high diffraction efficiency (the writer is aware of efficiencies greater than 98% for simple diffraction gratings produced by himself and a variety of other working groups worldwide).

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The main problems are associated with the collapse of the layer as the unexposed halide is removed by the fixer. This effect is extremely unhelpful to the efficiency of Lippmann layers and in transmission holograms will cause the movement of the interference patterns thus preventing effective phase conjugation of recorded images.

Surface Relief

And/Or

Layer Shrinks and
Plane Curves Over
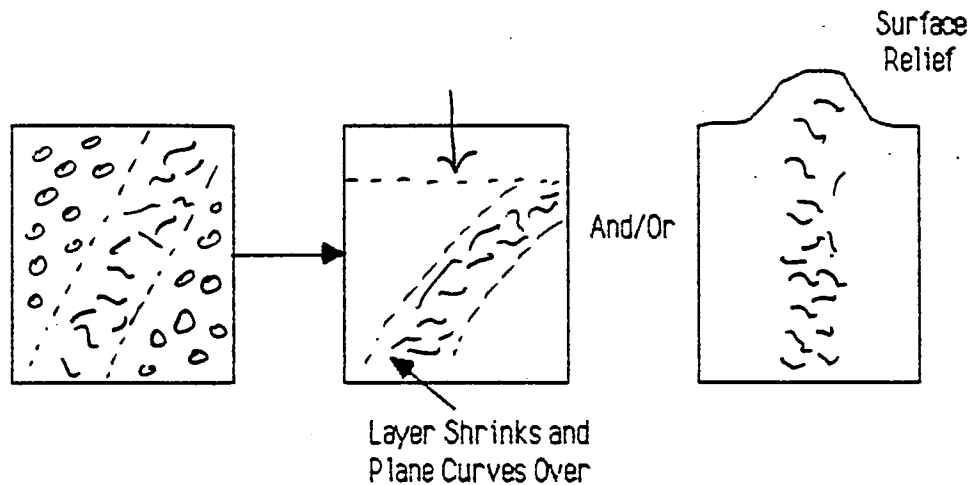
As the layer collapses, the orientation of the silver planes changes usually creating curved antinodal regions where flat planes were first created.

For simplistic recordings such as diffraction gratings, the topology is more helpful and the extremes of efficiency can be reached. Inevitably there is a tendency to create surface relief effects on the gelatin layer.

The reader is referred to the essential paper of Van Renesse and Bouts (8) for a discussion of the problem of phase modulation of holograms accompanying the rehalogenation process. They were the first to model in an effective way the rôle of the phase shifts induced by the conversion of the developed silver to a transparent compound. in fact, Van Renesse introduced an important empirical approximation to the Lorentz-Lorenz formula for the refractive index of the halides noting that the index can be described by the formula:

$$n = c\Sigma\alpha_i N_i + n_0 \qquad (3)$$

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where c and n_0 are curve fitting constants and α_i and N_i are the molecular polarizabilities and their respective number densities. This was derived from the rigorous classical formula:

$$n^2 = \frac{1 + \frac{8\pi}{3}\Sigma\alpha_i N_i}{1 - \frac{4\pi}{3}\Sigma\alpha_i N_i} \qquad (4)$$

From the approximate form they concluded that in fact the hologram is modulated by spatial variation of the sum $\Sigma\alpha_i N_i$. Much controversy has surrounded Van Renesse's comment that if a compound (e.g. Silver Ferrocyanide) can be found that matches the refractive index of the gelatin, then the hologram can be modulated without scatter. That this statement is correct in principle is obvious, but there has been some argument about the question of surface relief effects in the layer and the actual redistribution of the gelatin (Quintanilla et al (9)) when the layer is fixed. Nonetheless, there is little deviation from the broad principles outlined by Van Renesse and Bouts and their classic paper still provides a cornerstone of the subject.
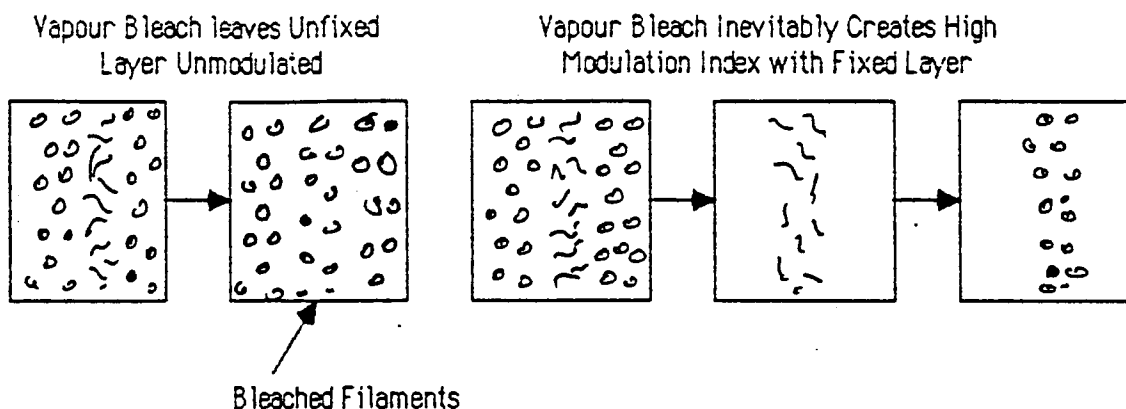
Actually, a much better approximation to the refractive index and one which is more sensible physically is of the form

$$n = 1 + 1.3904x + 1.0689x^2$$

where $\qquad x = (4\pi/3)\Sigma\alpha_i N_i$

*Here we note the essential **non-linearity** of the approximation. This result is derived from a quadratic fit and regression method. It covers the condition $n \to 1$ when $x \to 0$ as must be the case when there are no polarizable molecules left. Evidently, large changes of N due to physical transfer can introduce a non-linear response in the image!*

The bleach process is easily achieved, but is very subtle if the best results are required. Bleaches of the rehalogenating type can be aqueous or dry. The dry technique of Graube (10) is of great academic interest

since it inhibits any form of ionic migration during bleaching. When metallic silver is attacked by Bromine vapour, for example, then bleaching takes place, but modulation only appears if the image is first fixed.

Vapour Bleach leaves Unfixed
Layer Unmodulated

Vapour Bleach inevitably Creates High
Modulation Index with Fixed Layer

Bleached Filaments

Evidently, the non-appearance of modulation in unfixed layers treated by dry bleaching suggests that a diffusion transfer mechanism is present in aqueous bleach systems in which modulation can be observed in unfixed layers that are simply rehalogenated wet.

Most wet bleaches used for rehalogenation employ the following constituents:
   i)   An acid buffer,
   ii) An oxidising agent to ionize the silver,
   iii) An alkali halide to create the silver halide precipitate,
   iv) Other minor agents such as desensitizers.

The true rôle played by wet bleaches can be seen by the discussion in section (e).

d)   Physical transfer development; the I.E.D.T. process of Benton (1974).

In Benton's procedure, ionic transfer is encouraged by a 2 stage process of development.

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Exposure and Solution   Bleached
Direct Development Physical   Grains
       Development
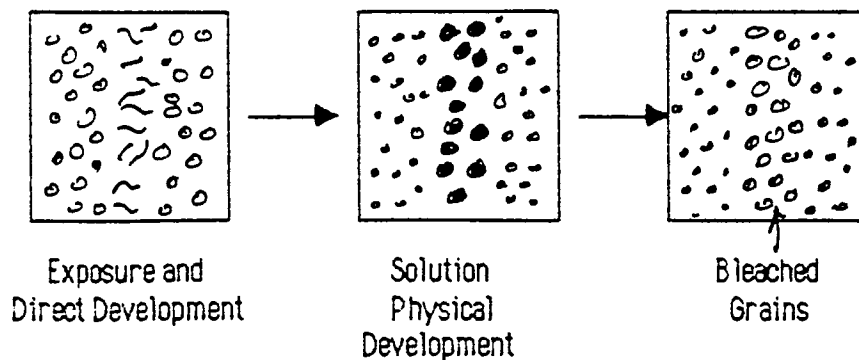
Benton's I.E.D.T. Process

The idea is that a direct development procedure is the precursor to the formation of enlarged spherical lumps of silver by physical development which is enabled by partial solution of the unexposed image. which then plates out on the exposed image. Finally, one bleaches the silver so formed thus creating a phase hologram. The formulations used are listed in the recipe sheet appendix.

A word of caution is necessary here because it would be all too easy to reverse the direction of transfer of the second development stage by the action of the bleach as is shown in section (e).

## e) Development (black silver) followed by wet rehalogenation

This method of modulation has now emerged as a clear winner in terms of overall efficiency of the image. It also helps to preserve the thickness of the recorded layer so as to avoid shrinkage of the interference image structure.

Its limitations have been highlighted by theoretical work of Phillips and recent practical work of Hariharan (to be published shortly) in which certain limitations of the method are highlighted.

It is evident that the performance of wet rehalogenating bleaches is subject to possible limitations at low spatial frequencies. Theory and experiment agree showing that this method is strongly dependent on the chemical composition of the bleach. Apparently the spatial frequency

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response of the bleached image can be subject to a low frequency cut off if there are limits imposed on the diffusion length of silver ions.

We see a particular problem in the recording of on-axis holographic lenses (zone plates) where the spatial frequency varies from zero at the centre to large values at the edge.

X ⟶   Phase Shift | Depends on X
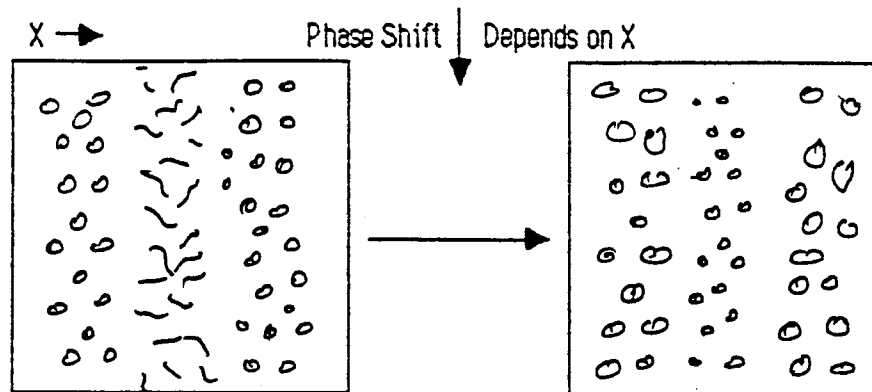
Wet Rehalogenation of Unfixed Layers Leads to Modulation:
Obviously Via Diffusion Transfer

In this mechanism, fixer is avoided but the image is modulated evidently by the diffusion transfer of halide during the **bleach** process. (Graube's dry technqiue fails to yield image modulation in the dry state). This technique was first publicised by Phillips et al (12) and has been revisited by many workers using different chemical formulations in the intervening years. The primary advantage of this technque is the minimal withdrawal of salts from the layer and hence the lack of induced collapse of the interference structure. The rôle of water is not generally appreciated but clearly if diffusion is invoked as an implicit mechanism of modulation, then the process of rehalogenation after fixing is complicated by the effect of unwanted diffusion.
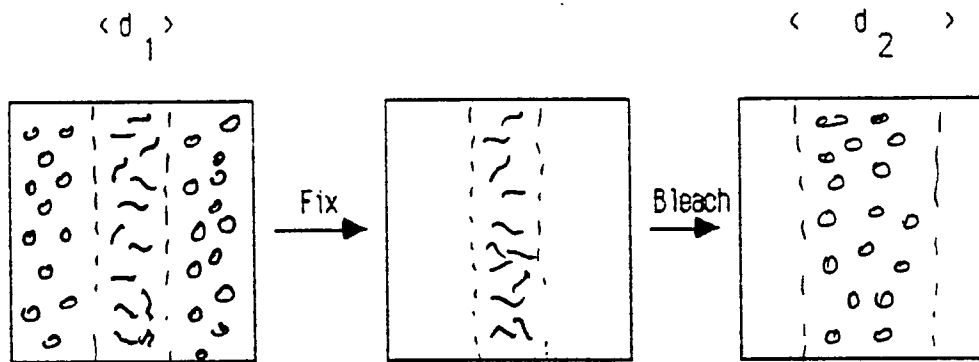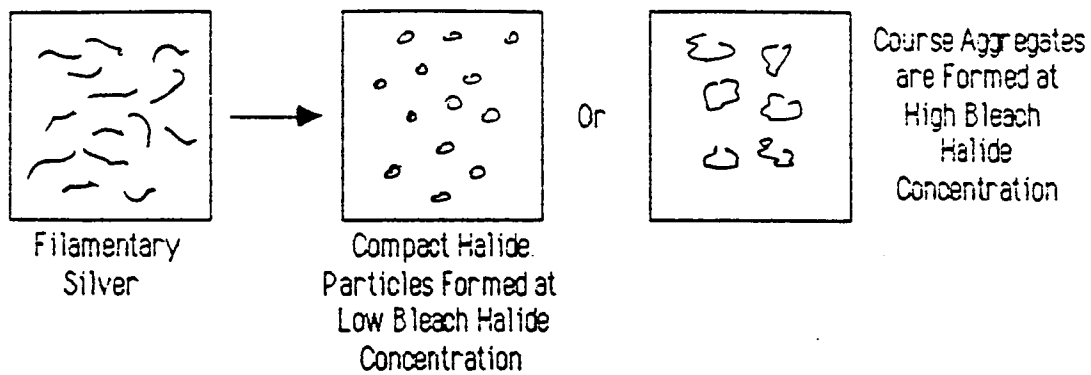
Initial Filamentary Zone Spreads out into Enlarged Zone due to Diffusion

$$d_2 > d_1$$

Evidently, a layer that is developed (black silver), fixed and wet rehalogenated will suffer from fringe contrast reduction due to migration of ions into the fixed interstices of the developed zones. Thus careful attention must be paid to wet bleaches so as not to confuse the issues.

It is easily shown that diffusion transfer is influenced by the acidity of the solution and by the Redox Potentials and concentration of the constituent active chemicals. The diffusion transfer effect seems not to work with populations of compact (colloidal) silver and thus the lack of enthusiasm of Soviet workers for the bleach process becomes understandable. It appears that the raw (unexposed) emulsion grain size needs to be of the order of $0.035\mu m$ or thereabouts in order that the mechanism can be initiated after development. In fact, if methods of development of even moderate grain size emulsions (c. $0.04\mu m$) are used to create **brown** rather than **black** silver, then the mechanism fails to take off.

The microscopy of the 'develop-bleach' process as we shall call it has been examined by Joly (13) and he has observed that the filamentary silver necks off during rehalogenation to form a compact form of halide particle: almost a reversal of the development process.

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Filamentary
Silver

Compact Halide
Particles Formed at
Low Bleach Halide
Concentration

Course Aggregates
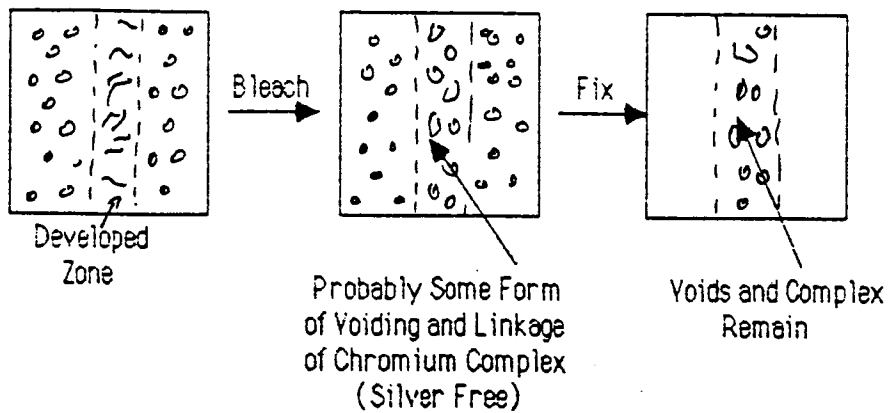are Formed at
High Bleach
Halide
Concentration

Or

However, as Joly points out, if the halide levels are too high then coarse aggregates with high light scatter are formed. In a recent paper Phillips and van der Werf (14) have reported reflectances for silver halide Lippmann layers of greater than 90% using the develop-bleach process. They found that other processes for modulation could not offer these levels of reflectance. In particular, some interesting questions have now been posed as to why the spatially incoherent light used in the results reported in the above paper created consistently higher diffraction efficiencies than the carefully produced laser recorded reflection gratings reported by Cooke and Ward (15).

f)   Development followed by tanning silver solvent action then fixing.

This system of processing is of great interest because it seeks to clear the emulsion totally of its grainy and hence scattering population. The method was propounded by Graver et al (16). Underlying the method is the desire to create an image by tanning modulation (possibly spatial modulation of attached dichromate complex or by voids) thus simulating the behaviour of dichromated gelatin, but making use of the sensitivity of the silver halides.

The method works tolerably well albeit with concommitent penalties of hermetic packaging to guarantee permanence of the result.
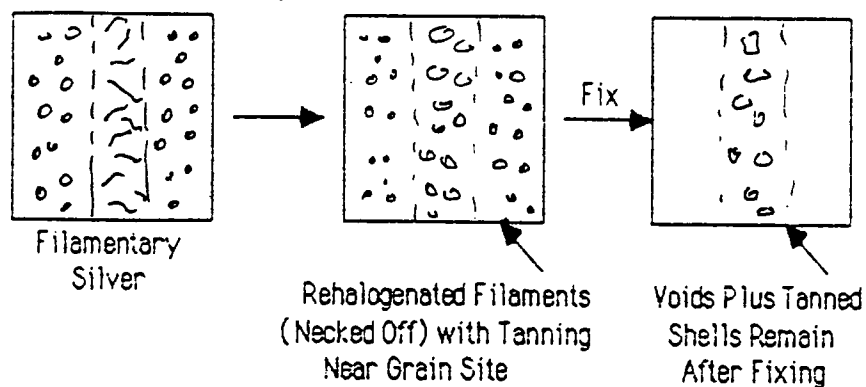
Developed Zone

Bleach → Probably Some Form of Voiding and Linkage of Chromium Complex (Silver Free)

Fix → Voids and Complex Remain

Efficiencies of 20-30% have been quoted for simplistic recording of holographic gratings.

g) Development followed by tanning rehalogenation of the silver then fixing.

This technique first published by Chang and Winnick (17) is seen as a variation on the previous theme although it is much more effective in achieving the required image modulation.

The wet rehalogenating bleach is formulated using the tanning agent Ammonium Dichromate. The tanning action obviously takes place whilst the layer is bulked up by the halide. One suspects that the superiority of efficiency over the Graver method is related to the formation of voids in the layer as the unwanted halide is removed by the fixer from the pre-tanned gelatin.

The Chang and Winnick methods has created diffraction gratings with over 75% diffraction efficiency. The same penalties apply to this method as to that of Graver and DCG technology in general: the layer must be hermetically packaged after completion to avoid the ingress of moisture and subsequent collapse.

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Filamentary
Silver

Rehalogenated Filaments
(Necked Off) with Tanning
Near Grain Site

Voids Plus Tanned
Shells Remain
After Fixing

Our checklist of what to do with the layer after sensitization is now complete as of today. The overall problem of how to label the exposed image in a conveniently different way to the unexposed image has been solved by a series of tricks each of which has its own subtleties.

Let us remember however that transmission and reflection gratings are cited with efficiencies of well over 90%, thus the story is one of considerable success.

h)   Something new and possibly very important!

At this stage of the paper, it has become clear that various forms of manipulation of the molecular population in the gelatin layer are the basis of the formation of the holographic modulation. We have shown a preference for methods which preserve the layer thickness by retention of the whole initial silver halide population.

Surely, there can be nothing which departs from these set paths varied though their directions might be?

In fact, a new possibility arises from the introduction of Ilford's proprietary Ilfoswell technique employing a solution which changes the structure of the gelatin by the addition of functional groups. Such ideas are not new in theory but the practice seems to have been neatly solved in this new preparation.

The Ilford method invokes a swelling of the gelatin layer at the end of processing in a bath which is then followed by a water wash. Thus the

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swelling action is permanent and not subject to washing out as with TEA or Sorbitol.

It is timely to propose that the combination of direct development (black silver) followed by fixing and rehalogenation using brominated methanol can now be finished off with a swellant which just restores the emulsion thickness. If this is possible, then unprecedented levels of flare free image modulation should be possible. This is because the migration of silver ion in the bleach can be avoided totally but without the unpleasant artefact of relief normally associated with the fixing stage of the process.

4. Areas requiring further understanding and progress.

One of the most important publications in relation to the halides is a recent paper by Johnson et al (18) in which the problem of reciprocity failure of silver halide emulsions is tackled in an instructive way. These workers ask why it is that successive and thus incoherently superposed exposures of a holographic layer do not all exhibit the same diffraction efficiency. Evidently, there is some pre-fogging of the layer by each previous exposure. This complex story is of great interest since it may help to unravel the mysteries and possibilities of point by point recording of holographic images.

The writer's view is that the true picture is probably a combination of underlying ideas in which the relative merit of black and brown silver development figures large. It must be borne in mind that black silver development is a high gain situation and that information will always be degraded with an excess of gain. We must look expectantly to progress in this field for truly if point by point recording can be acheved, the computer graphics industry can at last have a form of 3-D hard copy.

Perhaps we might also expect a significant interaction with this area of work from the important demands made by the nuclear physicists who are looking at bubble chamber holography. Here we should cite the work of Bjelkhagen (19) who has made significant advances in improving the sensitivity of high resolution emulsions under conditions of minimal available light levels. Thus his work makes it possible to consider

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exposure levels as low as $1\mu J/cm^2$ and further enhances the possibility of multiple low level exposures such as might be invoked in the point by point recording process. Irrespective of the sensitivity problem, however, we still have to pay due regard to the reciprocity failure difficulty outlined above.

5. Summary.

This review does not claim to be comprehensive in detail, but helps to focus attention on the key ideas that relate to our current knowledge of the use of silver halide holographic materials. The reader can explore the cited papers and their background bibliographies to enhance his knowledge. If there are other process techniques of significant current interest, then they will most certainly be related to the manipulative ideas cited in these references.

The recipes included in the Appendix are based on a large number of trials and should give trouble free results. The mysteries of proportions of chemicals used are briefly discussed but the results are based on trial and error and continual adjustment.

We have clearly seen that halide can be transferred in both the I.E.D.T. and develop-bleach process. The direction of transfer is most probably downhill to the unexposed image in the develop-bleach process and uphill from the unexposed to the exposed image in the I.E.D.T. case. **Thus we might say that transfer is downhill in bleaching and uphill in development.**

This difference is profound and probably puts the I.E.D.T. process on a pedestal clear of the pack. This conclusion is drawn because I.E.D.T. clearly involves an image enhancement process. The combination of Graube's dry bleach process with I.E.D.T. might prove formidable in terms of noise and image brightness.

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The silver halides are evidently a potent and helpful medium in which to record holographic images. The early pessimism relating to the problem of scatter from the grains has given way to considerable enthusiasm for the high efficiency and ease of use which these media permit.

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Appendix

THE RECIPES

1. DEVELOPER FOR PULSED LASER HOLOGRAPHY AS USED AT THE
    ROYAL COLLEGE OF ART (CREDIT TO HANS BJELKHAGEN)

        30 gms   ANHYDROUS SODIUM SULPHITE
         2 gms   PHENIDONE (PRE-DISSOLVED IN A
                              LITTLE METHANOL)
         8 gms   QUINOL
        60 gms   ANHYDROUS SODIUM CARBONATE
        1 litre DISTILLED WATER.

        USE AT 21-23°C.

        THIS DEVELOPER ENDOWS AGFA-GEVAERT'S 8E75HD
        MATERIAL WITH A SENSITIVITY $\approx$ 5 μJ/cm^2
        FOR A DEVELOPED DENSITY D $>$ 2.

2. DEVELOPER FOR SURFACE LATENT SITE DEVELOPMENT
    (AFTER JAMES - SEE REFERENCES)

                2 gms   METOL
               10 gms   ASCORBIC ACID
               60 gms   ANHYDROUS SODIUM CARBONATE
                1 litre DISTILLED WATER

USE AT 21-23°C. PROBABLY PREFERABLE TO MIX IN PART A
+ PART B FORMULATION. THUS ADD CARBONATE TO 500 ml H_2O
(PART B).

BEING SULPHITE FREE THE KEEPING PROPERTIES ARE TREACHEROUS
(ASCORBIC ACID DOES NOT KEEP WELL IN ALKALINE SOLUTION).
THE ABSENCE OF SULPHITE MINIMISES THE SOLUTION OF THE
HALIDE POPULATION.

3. DEVELOPER FOR STAINED REFLECTION HOLOGRAMS (AGFA MATERIALS)

PART A

5 gms   PYROGALLOL
500 ml DISTILLED WATER

PART B

60 gms ANHYDROUS SODIUM CARBONATE
500 ml DISTILLED WATER

USE AT 21-23°C.

MIX EQUAL PARTS JUST BEFORE USE. SOME PEOPLE THROW
THE RESULTING 'BROWN STEW' AWAY AFTER ONE USAGE,
OTHERS SAVE MONEY AND DEVELOP MORE THAN ONE PLATE!

4. DEVELOPER FOR TRANSMISSION HOLOGRAMS (AGFA-MATERIALS)

PART A

30 gms ANHYDROUS SODIUM SULPHITE
10 gms CATECHOL
 5 gms QUINOL
500 ml DISTILLED WATER

PART B

60 gms ANHYDROUS SODIUM CARBONATE
500 ml DISTILLED WATER.

MIX EQUAL PARTS FOR USE AT 21-23°C.

THIS DEVELOPER KEEPS REASONABLY IN THE DISH WHEN MIXED
BUT THE STAINING OF THE DISHES AND BENCHES BY THE OXIDISED
DEVELOPER IS AWFUL. THIS FORMULATION LIGHTLY TANS THE
EMULSION AND LEAVES A GLASSY FINISH IN THE DEVELOP-BLEACH
REGIME. (e).

5. <u>DEVELOPER FOR TRANSMISSION HOLOGRAMS (ILFORD MATERIALS)</u>

<u>PART A</u>

30 gms ANHYDROUS SODIUM SULPHITE
10 gms CATECHOL
 5 gms QUINOL
 5 gms POTASSIUM BROMIDE
500 ml DISTILLED WATER

<u>PART B</u>

10 gms SODIUM METABORATE
60 gms ANHYDROUS SODIUM CARBONATE
500 ml DISTILLED WATER

MIX EQUAL PARTS FOR USE.
USE AT 21-23°C.

HERE THE BROMIDE AND METABORATE ADDITIVES
CONTROL THE RAPID INDUCTION TENDENCY OF
CONVENTIONAL DEVELOPERS IN CONJUNCTION
WITH ILFORD MATERIALS. THIS PROBLEM CAN
CREATE SPLASH MARKS IN DEVELOPMENT WHICH
GET OUT OF HAND IN THE BLEACH.

6. DEVELOPER FOR STAINED REFLECTION HOLOGRAMS
    (ILFORD MATERIALS)

PART A

5 gms   PYROGALLOL
5 gms   POTASSIUM BROMIDE
500 ml DISTILLED WATER

PART B

10 gms SODIUM METABORATE
60 gms ANHYDROUS SODIUM CARBONATE

MIX EQUAL PARTS JUST BEFORE USE.
USE AT 21-23°C. NOTICE THE RESTRAINT OF
INDUCTION REQUIRED BY THE ILFORD MATERIALS.
ILFORD MATERIALS REQUIRE LESS STAIN THAN
AGFA (DUE TO TIGHTER CONTROL OF GRAIN SCATTER);
THIS BREW TAKES THIS INTO ACCOUNT.

7. <u>DEVELOPER FOR LOW NOISE TRANSMISSION HOLOGRAMS</u>
    <u>(N J PHILLIPS)</u>
    <u>(AGFA AND ILFORD MATERIALS)</u>

    30 gms ANHYDROUS SODIUM SULPHITE
    10 gms ASCORBIC ACID
     2 gms CHLOROHYDROQUINONE
            (CHLORQUINOL)
     5 gms POTASSIUM BROMIDE
    10 gms SODIUM METABORATE
    60 gms ANHYDROUS SODIUM CARBONATE
    1 litre DISTILLED WATER

    USE AT 21-23°C.

THIS DEVELOPER OVERCOMES THE PECULIAR PROPERTIES
OF ASCORBIC ACID AS A DEVELOPER. OVER EXPOSED
MATERIALS IN ASCORBIC ACID SHOW A TENDENCY FOR
IMAGE SOLUTION IN REHALOGENATING BLEACHES. THE
ORTHO CHLORO ADDITIVE OVERCOMES THIS PROBLEM.

8. FERRIC NITRATE BLEACH FOR TRANSMISSION HOLOGRAMS
   (PHILLIPS AND PORTER 1976)

           50-100 gms FERRIC NITRATE
              30 gms POTASSIUM BROMIDE
              1 litre DISTILLED WATER.

   THIS BLEACH KEEPS WELL, IS NON-TOXIC BUT NEEDS SOME
   ADJUSTMENT TO WORK EFFECTIVELY IN THE DEVELOP-BLEACH
   REGIME. TRY ADDING SOME DISODIUM E.D.T.A. SAY 15 gms
   TO ONE LITRE OF SOLUTION. THIS WILL PROMOTE PHYSICAL
   TRANSFER EFFECTS. YOU MAY THEN FIND THE SOLUTION
   SUITABLE FOR REFLECTION BLEACHING. FERRIC NITRATE IS
   IRRITATINGLY DELIQUESCENT. THIS MAKES IT DIFFICULT TO
   REMOVE FROM ITS BOTTLE WHEN IT HAS GOT DAMP. IT WAS
   FOR THIS REASON THAT FERRIC SULPHATE WAS SUBSTITUTED
   FOR THE FERRIC NITRATE IN THE ROYAL COLLEGE OF ART
   BLEACH.

9. <u>FOR REFERENCE</u>

<u>KODAK D19</u>

30-90	gms	ANHYDROUS SODIUM SULPHITE
2	gms	POTASSIUM BROMIDE
2	gms	METOL
8	gms	QUINOL
35-40	gms	ANHYDROUS SODIUM CARBONATE
1 litre		DISTILLED WATER

20-30°C.

A GOOD OLD STANDBY. HANS BJELKHAGEN FOUND THAT
THIS BREW + 2 gm PHENIDONE GAVE BEST DYNAMIC RANGE
OF A MULTIPLICITY OF DEVELOPERS FOR PULSED HOLOGRAPHY.
BE CAREFUL WITH THE HIGHER SULPHITE LEVELS HOWEVER
BECAUSE OF RISK OF HALIDE SOLUTION.

10. BLEACH FOR REFLECTION AND TRANSMISSION HOLOGRAMS

    2 gms   PARA BENZOQUINONE
    30 gms POTASSIUM BROMIDE
    1.5 gms BORIC ACID
    1 litre DISTILLED WATER

THIS WAS CREATED FOR REFLECTION HOLOGRAMS WITH
STAIN PRESERVED IN BLEACHING. WE CAUTION SUSPECT
TOXICITY OF THE FINELY DIVIDED SNUFF-LIKE POWDER
AND ITS IMPURITY. USE A FUME HOOD. AND DON'T
TAKE RISKS.

THIS BLEACH IS REALLY BEST USED ONCE OR TWICE AND
THEN THROWN AWAY. DO NOT ATTEMPT TO KEEP IT FOR
MORE THAN A WORKING DAY.

FILTER THE SOLUTION BEFORE USE. LUMPS OF P.B.Q.
WILL CAUSE FIXED OUT SPOTS ON THE HOLOGRAM.

11. BLEACH FOR TRANSMISSION AND REFLECTION HOLOGRAMS
     (N J PHILLIPS). USED AT THE ROYAL COLLEGE OF ART

     10 ml   CONC SULPHURIC ACID
     30 gms   FERRIC SULPHATE
     15 gms   DISODIUM E.D.T.A.
              (DIAMINOETHANE TETRAACETIC ACID).
              DISODIUM SALT
     30 gms   POTASSIUM BROMIDE
     1 litre DISTILLED WATER

A WAY OF MAKING THE E.D.T.A. COMPLEX WITH FERRIC ION
IN SITU. A GOOD RELIABLE BLEACH WITH GOOD KEEPING
PROPERTIES AND LOW TOXICITY. CAN BE TOPPED UP WITH
EXTRA DISTILLED WATER IF IT DRIES OUT. BLEACHED
RESULTS TEND TO BE PRINT OUT SENSITIVE SO WASH IN
FINAL BATH WITH 2% ACETIC ACID IN SOLUTION BEFORE
DRYING.

12. **FERRIC E.D.T.A. BLEACH FOR GENERAL USE**

     30-100 gms FERRIC-SODIUM-E.D.T.A.
        30 gms POTASSIUM BROMIDE
        10 ml CONC SULPHURIC ACID
     1 litre   DISTILLED WATER

THE CONCENTRATION OF FERRIC E.D.T.A. IS VARIED TO SUIT TASTES FOR SCATTER AND BRIGHTNESS (LOWER LEVEL - HIGHER SCATTER).

THIS IS A VERY LOW TOXICITY BLEACH WITH EXCELLENT KEEPING PROPERTIES. IT DOES TEND TO DE-STAIN PYROGALLOL DEVELOPED PLATES A LITTLE.

13. NON-AQUEOUS BLEACHING

    (AFTER GRAUBE)

    THE PURPOSE OF THIS BLEACH IS TO REHALOGENATE SILVER IN THE
    TOTAL ABSENCE OF PHYSICAL TRANSFER.

    METHODOLOGY:

    1. DEHYDRATE THE HOLOGRAM AS FOLLOWS.

        BATHE 50:50 METHANOL + WATER   3 mins.
        BATHE 100% METHANOL   3 mins.

        IMMEDIATELY TRANSFER TO

        1 litre METHANOL   (LIGHT BROWN
        + 3 mls LIQUID BROMINE   SOLUTION)

        CAUTION: EXTREME BIOLOGICAL HAZARD.
        WEAR GLOVES AND FACE MASK WHEN POURING LIQUID BROMINE
        INTO METHANOL. TO NEUTRALIZE THE BLEACH SOLUTION HAVE
        A BATH OF 50 gm ANHYDROUS SODIUM SULPHITE IN 1 litre of
        WATER READY. WHEN BLEACH IS USED IN TRAY THEN POUR
        NEUTRALIZING SOLUTION INTO IT BEFORE TIPPING RESIDUE AWAY.
        IF SPLASHES ON BODY OCCUR THEN IMMEDIATELY SOAK THAT PART
        IN NEUTRALIZING SOLUTION.

        N.B. WATER MUST NOT COME NEAR THE HOLOGRAM AFTER
        DEHYDRATION - THE LOW GRAIN GROWTH WILL BE NEGATED
        IF THIS HAPPENS.

14. SOLVENT BLEACHES

THESE ARE COMPOUNDED FROM ACIDIFIED SOLUTIONS OF: e.g.

(a)   0.5 gm POTASSIUM PERMANGANATE

+ 1 litre DISTILLED WATER

+ 0.25 ml CONC NITRIC ACID.

HOLOGRAM CAN BE WASHED AND CLEARED IN THE FOLLOWING SOLUTION

    ·   10 gm   SOD METABISULPHITE

         1 litre DISTILLED WATER.

(b) 2 gm   POTASSIUM DICHROMATE   \ TANNING
      2 ml   CONC SULPHURIC ACID   > SOLVENT
      1 litre DISTILLED WATER   J BLEACH.

THESE SILVER SOLVENTS ARE EFFECTIVE IN MODULATING THE HOLOGRAM BY REMOVING THE SILVER OF THE DEVELOPED IMAGE. THEY CAN CAUSE VOIDING IN THE EMULSION AND UNPLEASANT SCATTER. THE LEVELS OF ACID AND COMPLEXING AGENT SHOULD BE OPTIMIZED FOR THE SPECIFIC TASK. IF VOIDS DO NOT OCCUR THEN COLLAPSE OF THE LAYER PROBABLY DOES. THIS MAY BE HELPFUL FOR COLOUR TUNING BUT IT IS GENERALLY NOT HELPFUL TO MODULATION.

15. <u>BENTON'S I.E.D.T. PROCEDURE</u>

1. DIRECT DEVELOPMENT.

   2.5 gms   METOL
   10 gms   ASCORBIC ACID
   60 gms   ANHYDROUS SODIUM CARBONATE
   1 litre   DISTILLED WATER.

   21-23°C.

2. DIFFUSION TRANSFER BY PHYSICAL DEVELOPMENT.

   18.1 gms p-PHENYLENE DIAMINE DIHYDROCHLORIDE
   50 gms   ANHYDROUS SODIUM SULPHITE
   1 gm   POTASSIUM BROMIDE
   0.25 gm   SODIUM THIOCYANATE
   1 litre   DISTILLED WATER.

   ADJUST TO pH 8.0 WITH SODIUM METABORATE.
   N.B. p.P.D. DEVELOPER IS <u>TOXIC</u>.

3. BLEACH (NON PHYSICAL TRANSFER).

   e.g. BROMINE WATER

   or   NON-AQUEOUS BROMINE-METHANOL PROCESS.

N.B. I AM NOT TOO SURE THAT BROMINE WATER IS FREE FROM
     TRANSFER EFFECTS - USE THE NON-AQUEOUS BLEACH PROCESS
     FOR PREFERENCE.

16. GETTING RID OF STAINS ON DISHES, HANDS AND BENCHES

1. PREPARE OXIDISING SOLUTION

    2 ml   CONC SULPHURIC ACID
    0.5 gm   POTASSIUM PERMANGANATE
    1 litre WATER.

    SOAK THE AFFECTED AREAS IN THIS SOLUTION.

2. WASH AWAY SURPLUS SOLUTION (1) AND THEN
    SWAB DOWN WITH

    20 gm   SODIUM METABISULPHITE
    1 litre WATER.

    THE EFFECTS CAN BE REMARKABLE. BOTH WORKERS
    AND LABS LOOK SO MUCH MORE CIVILIZED AFTER USE.