HISTORY OF COLOR PHOTOGRAPHY

By

JOSEPH S. FRIEDMAN, Ph.D.

With Introduction and Appendix by
LLOYD E. VARDEN

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CHAPTER 26

THE TRANSFER PROCESSES

UNDER this heading could be grouped all the processes in which a color image is transferred from a matrix to another surface. The most successful uses of the technique are to be found in the Technicolor process for the making of color motion pictures, and the Eastman Wash-Off Relief process for the making of color prints. The study of the process is the study of the procedures for the preparation of a matrix. This is a scheme by which it becomes possible to differentiate image-bearing from non-image-bearing portions of a surface. For instance, we can treat a layer with a resist so that certain sections will not absorb dye or ink. The resist may be a tanning agent which prevents the imbibition of an aqueous solution. Or, it can be an agent which will cause a greasy ink to adhere. Matrices of this type are called planographic. Instead of treating portions of the surface to cause them to act differentially toward stains, the non-image portions could be completely removed. Matrices of this type are called reliefs. We will discuss the planographic matrices first.

About 1867, E. Edwards was concerned with the preparation of photogelatin transfer plates. He took out a number of patents in which he described the general method for their preparation and use (Eng. P. 2201/68, 2543/69, 2485/70, and 73/72). Generally, a gelatin layer was sensitized with dichromates, then exposed under a negative. The exposed portions became water-repellant, but ink-absorbent. This constituted the matrix. In a subsequent disclosure (Eng. P. 2799/71) he suggested that if the water (which was absorbed by the untanned portions and made them ink-repellant), contained aniline dyes, curious two-tone effects could be obtained, and both ink and dye would transfer. This was probably the first disclosure on record that a dye would transfer. Mr. Edwards recognized that he made a valuable contribution to the art, but outside of taking out a few more patents to secure his right to fame (U.S.P. 150946; Eng. P. 1362/75, 3453/75), he let the matter rest at this point.

The next advance came from Charles Cros (Fr. P. 139396) who rediscovered the idea, apparently in complete ignorance that it had been previously proposed. He called the procedure "Hydrotypie," indicating the use of aqueous solutions for the staining baths. The technique was further developed by L. Didier and commercialized by the German dye firm Meister, Lucius and Brüning (U.S.P. 885453; Eng. P. 7557/05; Fr. P. 337054; Ger. P. 176693) under the name "Pinatype."

In practice, a gelatin layer was sensitized by means of dichromate (cf. Chapter 25), then exposed under a positive. The exposed portions of the layer became tanned and water-repellant, so they would not imbibe water or certain dyes dissolved in the water. Hence the image corresponded to the unexposed portions. The sections which received partial exposure became partially tanned and these imbibed the water and dye to a corresponding degree. After staining, the matrix was brought in contact with a fresh gelatin surface. After a time the stain transferred to the new surface. Three such transfers in superposition gave the final color print. The matrices could be re-stained, and thus duplicate copies made.

Not all dyes could be used for this purpose. It must be remembered that as prepared above, the matrix consisted of an image of soft or untanned gelatin impressed upon a layer of hard gelatin. The dyes must stain the soft gelatin, but not the tanned, or if the staining is general, then the stain in the tanned portions must be readily removed while that in the soft portions must be relatively permanent. There are many dyes which have this property. A collection of such colors was at one time sold by the I.G. under the designation of Pina dyes, but their sale was discontinued about 1930. The chemical structure or the trade name of the dyes was never disclosed. The Eastman Kodak Company utilized similar dyes in their old discarded Kodachrome process (not to be confused with the present-day product of that name), but they also did not disclose the nature of the dyes. However, the patent files do give some information. The original Didier paper gives the following classes of dyes as suitable.

1. The Mikado dyes obtained from p-nitro-toluol-sulphonic acid,
2. Dyes made from dihydrothiotoluidin or primuline and their substitution products,
3. Sulphonated nigrosines and indulines,
4. Natural carmine,
5. Dianil dyes, and the
6. Arylido anthraquinone sulphonates

More specifically, natural carmine and the dye obtained when diazotized primuline sulphonic acid was coupled into naphthol disulphonic acid, could be used for the magenta; dianil yellow R for the yellow; and fast blue or induline sulphonic acid for cyan.

Special studies were made to determine what relationship existed between chemical constitution and the ability to stain gelatin. F. Curtis and P. Lemoult (Wall's "The History of Three-Color Photography," p. 397) found that the presence of sulphonic groups led to gelatin substantivity, while nitro groups had the opposite effect. Unfortunately, rhodamine and auramin were listed as nitro-containing dyes, which is not the case. They are basic dyes with no affinity for gelatin. A more practical solution was offered by L. Lemaire (*Brit. J. Phot.*, Vol. 58 (1911), p. 969). He recommended lanafuchsin 6B or brilliant lanafuchsin SL for the magenta, alizarin cyanol BF for the cyan, and paper yellow M or solid yellow 2GL and quinoline yellow for the yellow. The dyes were in one per cent solution. They were brushed on the matrices. Other dyes which have this preferential staining action, or dyes which would stain tanned gelatin in preference to the untanned, are disclosed in some of the patents dealing with the formation of screens (cf. Chapters 12 and 13).

Complete working directions for pinatype were contained in the "Pina Manual," a pamphlet issued by the Agfa company. The separations are first converted into positive transparencies. These, with the exception of the yellow, should be very soft, hence they might be made upon a color-blind negative material. The yellow image should be developed fairly hard. If it is desired to use transparency plates, then, the developer should be compounded along the lines outlined by J. S. Friedman (cf. discussion of the Brewster process, Chapter 21).

The printing plates are specially coated gelatin plates, but there is no reason to doubt that almost any plate or film could be used, if the silver halide emulsion were first fixed out with plain hypo, then washed thoroughly to remove all traces of this agent. If the transparencies are somewhat hard, it might be preferable to leave the emulsion in the film. This will control the penetration of the printing light into the print plate. Sensitization is accomplished by bathing in 2½ per cent ammonium dichromate, or in any of the baths mentioned in Chapter 25. The time of treatment is three to five minutes at 15 C, after which they should be drained thoroughly, and put up to dry. This operation can be carried out in diffused yellow light.

The exposures are made through the positive transparencies, the source of illumination being an arc light or bright sunlight. Mazda light would prolong the time unduly. The plates are fixed by merely washing them in water until all the unexposed dichromate is removed, after which they may either be dried, or immediately stained. If the material used still contains silver bromide, this may be fixed out by plain hypo, followed by a thorough washing.

The matrices are stained in suitable dye baths, which are as follows:

Cyan	
Pinatype blue F	2–3 parts
Water	100 parts
Magenta	
Pinatype red F	3–4 parts
Ammonia	3–5 parts
Water	100 parts
Yellow	
Pinatype yellow F	3 parts
Water, hot	100 parts
Cool before using.	

The matrices are treated in these baths for a period of ten minutes. The excess is washed in running water. Washing should be continued until the whites are clean. The image is best examined by placing it on a white surface, such as a white opaque glass or an enameled tray. Too low a contrast may be due to too short an exposure which did not harden the highlights to enable the shadows sufficient time to absorb enough dye. Overexposure leads to loss of highlight detail.

After dyeing and washing to satisfaction, the matrix is brought into contact with a thoroughly wet sheet of transfer paper. A process of preparing such a paper is described below, when the subject of Wash-Off Relief is discussed. Contact between the two is established quickly, but absolute care must be maintained that once contact is established, there should be no relative motion between transfer paper and matrix. The dye transfer starts immediately, and if any motion occurs, a blurred image will result. The time should be sufficient to allow a complete transfer of the dye. Any air bubbles will be indicated by white specks in the print. After transfer, the matrix should be re-dyed. This time a much shorter period is required both for dyeing and for transfer. It is best to leave the yellow transfer for the last, since then registry will be easier. After the three transfers have been made in registry upon the same sheet of transfer paper, it can be treated with a three-per-cent solution of copper sulphate. This will tend to mordant the dye in place.

These disclosures evoked a considerable interest, but most of the published and patented modifications dealt with slight variations in the formulas, or with the use of this procedure in combination with some other. However, some writers did contain themselves and dealt only with pinatype. L. Vidal (*Brit. J. Phot.*, Vol. 53 (1906), p. 390; Vol. 54 (1907), *Col. Supp.*, p. 9) suggested a procedure which he claimed gave more brilliant results. A glass plate is first coated with collodion, then with gelatin. The gelatin layer is sensitized, exposed, washed, then freed from the brown chromium stain by a treatment with bisulphite, washed, and finally dried. The dry plate is stained and washed in the manner described above, after which it is dried, then recoated with gelatin, sensitized, printed in registry through a second separation, fixed, stained, etc., until three images have been formed. The final act is to coat again with gelatin, set, and bring in contact with a sheet of gelatinized backing paper. When this is dried, the print can be stripped from the glass by merely cutting around the edges with a sharp knife. If plate glass is used, the print will have a high polish. If a ground glass is used, the finish will be mat.

L. Didier (*Jahrbuch*, Vol. 19 (1905), p. 343; *Brit. J. Phot.*, Vol. 54 (1907) *Col. Supp.*, p. 43) made an interesting modification. The separation negatives were converted into normal separation positives. These should be fairly dense, with clean whites. The yellow should be printed heavier than the other two. Development is effected in a non-tanning developer. The positives are then sensitized with dichromate placed in contact with a sheet of printing-out paper, and exposed until details appear in the shadows. The printing-out paper serves merely as an actinometer. It is readily seen that by this procedure the gelatin in situ with the silver remains soft to the extent of the image density. After washing the plate free from unreacted dichromate, the silver is removed by the action of Farmer's reducer, leaving a pinatype matrix of pure gelatin.

Another novelty was proposed by G. Engelken. He did for this procedure what Manly did for carbro. He tanned the gelatin in situ with the silver by treatment with an ozobrome bleach (cf. Chapter 25). The tanned portions become immune to the action of pina dyes (*Jahrbuch*, Vol. 21 (1906), p. 453; *Brit. J. Phot.*, Vol. 56 (1909), *Col. Supp.*, p. 36). F. W. Donisthorpe accomplished the same result with an uranium toner, which also tanned the gelatin in situ with a silver image (U.S.P. 923030, 1517200; Eng. P. 13874/07; 5641/08, 7087/08, 158021; Ger. P. 219188, 360550; Fr. P. 518229). Several alternative baths were given. The negative silver image was first treated with

Uranium nitrate	1 part
Potassium ferricyanide	1 part
Water	45 parts

for ten minutes, after which it was treated with

Ferric chloride	1 part
Glycerin	1 part
Water	50 parts

Another possibility was to bleach the image in

Lead nitrate	4 parts
Potassium ferricyanide	6 parts
Acetic acid	2 parts
Glycerin	1 part
Water	100 parts

for ten minutes, then bathe in 2½ per cent sodium sulphide solution until completely toned. The preferred bath, however, was the following:

Vanadium chloride	2 parts
Potassium ferricyanide	2 parts
Ferric chloride	1 part
Glycerin	1 part
Ferric oxalate	1 part
Saturated oxalic acid	100 parts
Water	900 parts

If the dye did not take very evenly a remedy was to add more oxalic acid.

A similar idea was utilized by J. E. Thornton (U.S.P. 1921050; Eng. P. 25084/12, 339296). He disclosed several bleach formulas that tanned the gelatin sufficiently to be suitable for use with pinatype dyes. The image can be treated with any of the following:

1.	Potassium dichromate	10 parts
	Potassium alum, 10% solution	5 parts
	Water	250 parts
2.	Copper sulphate	2 parts
	Potassium bromide	1 part
	Potassium dichromate	1 part
	Water	100 parts
3.	Cupric bromide	50 parts
	Potassium dichromate	1 part
	Water	1000 parts
4.	This is formed by mixing equal parts of *A* and *B*	
(*A*).	Potassium ferricyanide	37½ parts
	Potassium bromide	36¼ parts
	Potassium dichromate	37½ parts
	Acetic acid	10 parts
	Water to	1000 parts
(*B*).	Potassium alum	50 parts
	Water to	1000 parts

It is to be noted that the first bath is a typical carbro sensitizer, while the second is a typical bromoil bleach. After bleaching, the print is washed in running water for one minute, treated with a ten per cent sodium sulphite solution, fixed in acid hypo, washed well, then stained with pinatype dyes such as platinum black or nigrosine. For color, the proper secondaries should be used.

Much along the same lines was the process Eastman tentatively introduced shortly after World War I, under the name of Kodachrome. This is not to be confused with the Kodachrome of 1935, which adopted the old name, but which bore no other resemblance to that process. The first Kodachrome was the invention of J. G. Capstaff (U.S.P. 1196080; Eng. P. 13429/15; Ger. P. 279802; Fr. P. 479796, 479798). The printing must be done through positives. The negative silver is developed with an MQ developer, after which it is washed for ten minutes. It is then bleached in a solution made by mixing equal parts of *A* and *B*:

(*A*).	Potassium ferricyanide	37.5 parts
	Potassium bromide	56.25 parts
	Potassium bichromate	37.5 parts
	Acetic acid	10 parts
	Water to	1000 parts
(*B*).	Potassium alum	50 parts
	Water to	1000 parts

Fixation should be in an acid, but alum-free hypo. A further wash of twenty minutes is followed by a bath of five per cent ammonia for three minutes, then a wash for five minutes, after which the plate was dried. Drying was the ticklish part of the procedure, and success or failure hinged on the ability to achieve this in a uniform and thorough manner. Special dyes known as Kodachrome red and Kodachrome green were used for staining, these being evidently pinatype colors since only the non-tanned portions of the plate absorbed them. But the names or formulas were never disclosed.

Somewhat later, Capstaff modified the procedure. In the original Kodachrome the non-image portions of the plate were tanned. This meant that printing was to be done from positives, a handicap since it involved another remove from the original. In the newer technique, the image was the silver-bearing portion of the plate. To accomplish this, Capstaff utilized an idea that had already found application in the photomechanical printing trade. Gelatin printing surfaces were prepared by sensitizing a gelatin-coated plate with ferric chloride and tartaric acid. This treatment tanned the gelatin so that it became completely ink-receptive and water-repellant. Upon exposure to light under a negative, the ferric ion became reduced to the ferrous state. This no longer had any specific action on the gelatin (Eng. P. 586/63; cf. also article by J. Joe, *Brit. J. Phot.*, Vol. 60 (1913), p. 250). By this means an imagewise de-tanning of the gelatin took place. Formulas and working directions for the technique are described in the chapter titled: "The Iron Processes" in Wall and Jordan's "Photographic Facts and Formulas."

The Capstaff modification consisted in treating a normal positive image with a bleach containing ferric chloride and tartaric acid. It was not necessary to fix the plate after development, since another fixation is required after the bleach. As recommended by Capstaff, the procedure was as follows (U.S.P. 1315464). Positive images were printed from separation negatives. These were developed, washed, then bleached in

Ferric chloride	100 parts
Tartaric acid	30 parts
Water to	1000 parts

After bleaching, the plates were fixed, washed, and dyed, using presumably the Kodachrome dyes or their equivalents, the pinatype dyes.

In more recent times J. E. Thornton utilized a planographic matrix and pinatype dyes, for the preparation of color films (U.S.P. 1921050; Eng. P. 339296). The negative silver images, formed on a duplitized film stock, are developed in a non-tanning developer, then bleached in a bromoil bleach or a carbro sensitizing solution, such as the one made by mixing equal parts of *A* and *B*.

(*A*).	Potassium ferricyanide	37.5 parts
	Potassium bromide	36.25 parts
	Potassium dichromate	37.5 parts
	Acetic acid	10 parts
	Water to	1000 parts

(*B*). Potassium alum	50 parts
Water to	1000 parts

The bleached prints are washed, then fixed in a bisulphite hypo made by mixing equal parts of 25 per cent hypo and 40 per cent sodium bisulphite solution. Washing and drying prepares the film for the dyeing operation. In accompanying patents, Mr. Thornton discloses the preparation of the duplitized material (Eng. P. 339319, 339321). In other patents (Eng. P. 316331, 316367) he mentions pinatype procedure for making one or more of the part images.

A somewhat different approach to this problem is disclosed by L. T. Troland (U.S.P. 2013116; Eng. P. 377033). The matrix is hardened generally, but is softened imagewise. This is accomplished by the use of either of the following bleaches:

1. Copper sulphate	20 parts
Potassium bromide	1 part
Nitric acid	2 parts
Potassium perborate	5 parts
Water to	1000 parts

or

2. Potassium ferricyanide	1 part
Potassium permanganate	1 part
Water to	100 parts

If the second of the bleaches is used, the film must be cleared first in dilute hydrochloric acid, then in 10 per cent sodium bisulphite. Here it is the image bearing portions which are softened, hence the matrix silver image must be a positive. The I.G. (Eng. P. 447488) did just the opposite. The matrix was first given a general tanning, then the areas carrying the silver image were further tanned so that these portions would not absorb the dye. Hence the silver matrix image must be a negative.

Bromoil and the photo-gelatin processes also use planographic matrices. But now it is the tanned gelatin portions which become stained. The coloring matters used are special greasy inks, litho or collotype. Wall and Jordan's "Photographic Facts and Formulas" devotes a section to this subject, and many books have been published which deal exclusively with bromoil and bromoil transfer, so we will not go into any great discussion of the technique at this point. But we must mention one modification described by Wall. The print or enlargement should be developed with a non-tanning developer fixed in plain hypo, washed, then bleached in

Potassium bromide	10 parts
Copper sulphate	15 parts
Potassium dichromate	5 parts
Water to	1000 parts

To this should be added just sufficient hydrochloric acid to form a clear solution. A large excess of acid is to be avoided for the reason noted in the chapter on carbon and carbro. When completely bleached, the paper is washed well, then treated with a one per cent sulphuric acid solution. This will remove any residual yellow stain in the film. Wash to remove excess acid, fix in plain hypo, wash well to remove excess hypo, then swell differentially by treatment for ten minutes with

Glycerin	1 part
Water	2 parts

The matrix is placed face up on a glass plate, and it is rolled down with a squeegee. This removes the surface excess of water. The inking is done with a roller.

So much for the planographic procedures. We now turn our attention to the relief matrices. Here image density is translated into gelatin thickness. Four distinct methods are available to accomplish this. One is patterned after carbon, the others tan the gelatin imagewise in connection with a silver image, but all of them utilize a silver-halide emulsion. Certain developing agents, when oxidized, unite with gelatin to tan it. This rather direct method is the basis for the Technicolor process. On the other hand, Eastman, in its Wash-Off Relief procedure, treats the silver image with acid dichromate, and achieves imagewise tanning at the same time. It is also possible to achieve imagewise detanning as was pointed out above.

Carbon technique for the preparation of a relief matrix was first suggested by E. Sanger-Shepherd and O. M. Bartlett (U.S.P. 728310; Eng. P. 24234/02; Fr. P. 329526; Ger. P. 161519). A sheet of celluloid was coated with gelatin and sensitized with dichromate. It was exposed through the support, under a negative. After exposure, it was developed in hot water. The unexposed, hence untanned gelatin, dissolved away, leaving an image on the celluloid in the form of a relief composed of tanned gelatin. This was stained with aniline dyes, and the stained side brought in contact with a sheet of gelatinized paper, previously soaked in water. After a while it was found that the aniline dye transferred from the matrix to the "blank," as the gelatinized paper was called. The men also pointed out in their disclosure that duplications become simple by this procedure. As L. Vidal pointed out (*Mon. Phot.*, Vol. 42 (1913), p. 6), this technique differs from that of Cros only in the minor detail that a relief matrix is used, while Cros utilized a planographic matrix.

Once the idea of carbon reliefs was proposed, others began to use it. J. H. Smith and W. Merckens (Eng. P. 7217/07; U.S.P. 885066; Fr. P. 376062; Ger. P. 209444) transferred to a collodion surface instead of gelatin. Ives, especially, did considerable work in this field, mainly in the development of simple dodges to give better control, to extend the range of the available dyes, etc. His patents and writings could well serve as a text on this subject (U.S.P. 1106816, 1160288, 1121184; Eng. P. 15823/14; Fr. P. 463737; Ger. P. 308030). He evidently was the first person to treat the gelatin in the blank with a dye-acceptor or mordant. He also emphasized the influence of the pH of the dye bath upon the contrast of the dyed matrix, a fact previously disclosed by von Hübl (*Brit. J. Phot.*, Vol. 46 (1899), p. 409, 470, 537). These ideas are now standard practice in all imbibition schemes.

Making the matrix by the carbon technique severely restricted the scope, since only contact printing was permissible. It is not surprising, therefore, to find that this application of carbon did not become popular, nor affect in any way any of the other schemes which allowed the use of a normal silver image. Some of these preceded carbon by a considerable time. One such scheme was the developed relief, a technique brought to a high degree of precision by Technicolor.

Wall traces its history back to J. W. Swan, who prepared photo-relief plates by development with pyro-ammonia in 1879 (Eng. P. 2969/79), but these were evidently not relief images. It was L. Warnerke who first made relief matrices in this manner (Eng. P. 1436/81). He used a standard pyro-ammonia developer, but left all the sulphite from the bath. In the absence of sulphite, the oxidized pyro reacted with the gelatin, to tan it. Some time later *Silbermann* pointed out that the degree of tanning could be controlled by the addition of some sulphite (*Silbermann*, Vol. 2, p. 141). He also pointed out that other developing agents had similar properties. Hydroquinone and amidol gave strong reliefs. Metol and diaminophenol gave weaker ones, while glycin gave no relief at all.

Before discussing the details of such procedures it would be well to examine the characteristics of the matrix emulsions. This must be a fine-grained silver-halide emulsion, suspended in soft gelatin. The matrix material must wash away from non-image portions, leaving no trace of substance capable of absorbing color. In the pure whites, the matrix gelatin must leave bare celluloid or substratum. This creates a problem, for the ordinary substratum contains tanned gelatin. G. F. Nadeau (U.S.P. 2169004) suggested a low dye-retaining substratum. Another problem which arises from the fact that most substrating solutions contain acetic acid, is that the acid destroys the sensitivity of the emulsion in that region. This means that the emulsion adjacent to the film base is least sensitive, and it is highly desirable that it be most sensitive there. M. W. Seymour (U.S.P. 1946640; Eng. P. 381787) discussed this phase of the problem, which, however, need not concern the average technician since matrix material is an article of commerce.

The control of the contrast of the final image can be accomplished in the manufacture of the matrix. The use of yellow dyes to insure a very low relief has been long recognized. The Jos Pé company sought to control the shape of the H & D curve, especially the toe regions, by mixing five per-cent of a fast negative emulsion to the slow matrix (Eng. P. 327283). This was achieved by E. A. Weaver by pre-exposing the emulsion to just below fog level (Eng. P. 263331). Another important control of relief depth was obtained by Technicolor in the following manner (U.S.P. 2044864; Eng. P. 385293). The yellow dyed emulsion was sensitized to the green. When high contrasts were desired, the printing was done with green light. By judicious choice of filters it became possible to get any contrast between the two extremes.

This dodge was by no means novel with Technicolor. It was disclosed first by R. Fischer in 1912, but in a slightly different form. He mixed a very contrasty color-blind emulsion with a flat orthochromatic one. By a choice of filters, it became possible to obtain any contrast between the two extremes. Varigam paper of more recent times utilizes the same principle.

Other methods to control the contrast of the dye image were to add photographically inert substances to the emulsion. H. Piloty (U.S.P. 1586697) added agents which retarded the dye transfer from the matrix. The opposite effect was achieved by F. Janzen (U.S.P. 1613515) who added substances which increased the ability of the matrix to absorb dyes. The I.G. added pigments (U.S.P. 2181485; Eng. P. 443111, 499758). The Jos Pé Company added dyes (Eng. P. 330997).

In tanning development the degree of tanning could be controlled by the amount of sulphite present in the developer. This was a general phenomenon that was independent of the particular agent used. Different experimenters preferred different developing agents, but soon the field narrowed down to two agents, pyrogallol and pyrocatechin. For some reason Wall showed a strong preference for hydroquinone, but in this he was practically alone. In his excellent book, "Practical Color Photography," he gives the following formulas for developers that tan the gelatin in situ with the developed image:

1.	Metol	1.5 parts
	Hydroquinone	1.5 parts
	Sodium sulphite	2.0 parts
	Sodium carbonate	17.5 parts
	Potassium bromide	1.5 parts
	Water to	1000 parts

2.	Hydroquinone	4.0 parts
	Sodium sulphite	2.0 parts
	Sodium carbonate	15.5 parts
	Potassium bromide	1.0 part
	Water to	1000 parts

In this formula the carbonate could be replaced with six parts of caustic soda.

3.	Pyrocatechin	2.0 parts
	Sodium sulphite	2.0 parts
	Sodium hydroxide	1.5 parts
	Potassium bromide	1.0 part
	Water to	1000 parts

Mr. Wall gives a pyro formula which contains a relatively large quantity of sulphite:

Pyrogallol	2.0 parts
Sodium sulphite	16.0 parts
Sodium carbonate	8.0 parts
Potassium bromide	0.5 part
Water to	1000 parts

Mr. Wall had an excellent opportunity to observe the action of pyrogallol at the Technicolor Laboratories. This organization brought the art of matrix making by the use of tanning developers to a high degree of precision. The formula used by Technicolor was disclosed in a patent issued to Dr. L. T. Troland (U.S.P. 1535700; Eng. P. 204034; Fr. P. 570076; Ger. P. 400951).

Pyrogallol	8.2 parts
Citric acid	0.2 part
Potassium bromide	4.0 parts
Sodium hydroxide	3.4 parts
Ammonium chloride	1.7 parts
Water to	1000 parts

This is a somewhat more contrasty developer than the one disclosed in a later patent issued to L. T. Troland and R. D. Eaton (U.S.P. 1919673; Eng. P. 392785), which described the entire matrix procedure. The developer formula was:

Pyrogallol	8.0 parts
Sodium hydroxide	3.0 parts
Ammonium chloride	1.5 parts
Potassium bromide	1.5 parts
Citric acid	0.2 part
Water to	1000 parts

The working bath was compounded from two stock solutions, one containing the caustic soda, the other containing the remaining ingredients except ammonium chloride. This was added to the developer in the form of a powder. Since the keeping qualities of pyrogallol are very poor, except in strongly acid solutions, the stock containing this ingredient was made up in a highly concentrated form, which required at least a twenty-fold dilution for use. The high acidity was obtained by addition of citric acid, which explains its presence in the formula. Mr. Wall, in his discussion of this formula ("History of Three-Color Photography," p. 356), points out the lack of originality in the use of a mixture of ammonium chloride and caustic. He writes: "Obviously this is nothing more than Warnerke's original developer when it acts. The setting free of ammonia from a halide by caustic alkali has been known for many years." But the action of a developer compounded with straight ammonia is quite different from one in which the ammonia is generated by the action of an alkali upon an ammonium salt. The reaction

$$NaOH + NH_4Cl \rightarrow NaCl + NH_4OH$$

requires the presence of forty parts of alkali for fifty-two parts of sal ammoniac. But in the two formulas disclosed by Dr. Troland, the alkali is present in much greater proportions. The alkalinity of such a bath would be much greater than in one containing only ammonia. Also the change in alkalinity as the ammonia evaporated would be made less. Therefore the solution is somewhat stabilized against change should it be used for an appreciable length of time. There may therefore be definite advantages in the use of a Troland type of developer over that of Warnerke. From experiences gained while a member of the Technicolor staff, I can say that cleaner reliefs result from the Troland formula. If there should be any criticism leveled at the formula, a better one would be the failure to use ammonium bromide instead of potassium bromide. This would obviate the need to use potassium bromide as a restrainer. The presence of chloride ions is practically of no value in a developer that is intended for use with iodobromide emulsions.

After development of the silver image, the matrix was washed for a definite length of time in water, whose temperature was controlled to close limits. The tanning is a result of the reaction that takes place near the places where the pyro is oxidized, i.e., adjacent to the silver of the image. It has always been considered that this reaction is an instantaneous one, occurring at the time that the oxidized pyro is formed. It has also been assumed that the reaction between the two is complete. However, against these ideas, may be brought the fact that the tanning action continues to take place during the wash period following development. This can be tested by the growth of the relief image with increased time of washing. Such image growth can be detected even after twenty-four hours. Whether the growth is dependent upon the diffusion of the oxidized pyro from the locus of its formation, or whether it is an "age" effect, has never been determined. For this reason it is very important that the elapsed time from entrance into developer to entrance into the hot water etch bath be strictly controlled.

The further processing of the matrix is open to a great variety of procedures. Where it is important to recover the silver, the matrix is bleached, washed, and fixed before it is etched. Otherwise, it can be etched immediately after the developer wash. The bleaching is accomplished by use of an oxidizing agent. Technicolor prefers to use a fourteen per-cent solution of potassium ferricyanide to convert the silver into fixable form. This is very convenient for continuous long-time operation, but becomes expensive when only occasional matrices are made. If some bromide be added, the concentration of ferri can be materially reduced, a suitable solution being:

Potassium ferricyanide	15 parts
Potassium bromide	15 parts
Water to	1000 parts

It is also possible to use acid dichromate or cupric chloride solutions, but the ferricyanide baths are the most convenient. The bleach is followed by a wash, then by plain hypo, after which it is treated to form the relief.

This is done by placing the matrix in hot water whose temperature is maintained at 120 F. After a minute, the untanned gelatin will dissolve away. It should be kept in this bath until no more dissolution of the gelatin takes place. If the matrix has not been fixed out before the hot water etch, it becomes easy to determine the end point, when no more cloudy material is washed away. Otherwise, trial and error will set a time limit. At this stage the remaining gelatin, in the form of a relief image, is swollen and very delicate. It must be set immediately. In carbro, the technique of setting is to plunge the image into cold water. A much better practice is to dehydrate it by treatment with strong alcohol, thus setting it chemically.

Procedures for the preparation of matrices using tanning developers are disclosed also by the Daylight Film Corporation (Eng. P. 187638; Fr. P. 539828), R. John (U.S.P. 1374853, 1417328, 1778139), the I.G. (U.S.P. 1453258; Eng. P. 172342; Fr. P. 518526), and the Jos Pé Company, who operate under the Koppmann disclosures (Ger. P. 309193, 310037, 310038, 358093, 358149, 358165, 358166, 358167, 358193, 395805). Most of these add nothing new to the practice, but Mr. Koppmann introduced one variation which has been also propounded by J. G. Capstaff (U.S.P. 1525766). This was to expose the matrix in the normal manner, develop with a non-tanning developer, expose the remaining grains, and develop these with a tanning developer. The gelatin beneath the primary image becomes tanned. Since this corresponds to a reversal, the primary image must be a negative, hence the exposure must be made through positives, or the original negatives could be used.

Tanning developers were never used to any great extent by the amateur technician. He preferred to use the tanning bleach processes. Probably this was due to the fact that Eastman introduced him to Wash-Off Relief, which utilized an acid dichromate bleach to yield imagewise tanning of the gelatin. The reactions are identically those involved in carbro, except that the relief image is treated as a matrix. Historically we can trace the technique to E. Howard Farmer (Eng. P. 17773/99) who discovered that dichromate solutions acted upon a silver image to form chromic salts, which then united with the gelatin to form insoluble gelatin in situ with the silver. This was a remarkable discovery, one of the few really basic reactions known to photographic chemists. He described the reaction as catalyzed by the silver. If a plate or film containing a silver image be immersed for a few seconds in a twenty per cent ammonium dichromate solution, an imagewise tanning of the gelatin results. These tanned images show all the properties of a light-reduced dichromate sensitized material.

The importance to photographers of this observation by Farmer lies in the fact that it now became possible to duplicate with silver all the effects produced by light upon dichromate sensitized tissue. Carbon has been universally recognized as one of the finest of reproduction media. Its use was limited considerably by the fact that only contact printing was possible. With this discovery it became possible to obtain carbon print quality from a normal silver image. Coupled with carbro, it makes it possible to replace light by a silver image. This can be an enlargement from a small negative. Carbro and its predecessor, the Raydex process, obviously were based upon this discovery.

Immediately after this disclosure an animated discussion arose as to the exact chemistry involved. This has never been quite cleared up to the satisfaction of everyone, but there is little doubt that the same principles are involved here as in the tanning of leather. This we have discussed in detail in the chapter dealing with carbon and carbro, so there is no need to repeat it at this point.

Farmer failed to mention that the silver-image-bearing film could be pigmented. This remarkably original discovery came considerably later, to be exact in 1902, when Riebensahm and Posseldt were issued a German patent covering this extension (Ger. P. 153439). A corresponding English patent was granted curiously enough to Riebensahm and Koppmann (Eng. P. 808/04). There does not seem to be an American patent, which somehow restores one's faith in our patent system. To overcome the loss of speed incident to the use of pigmented gelatin as a carrier for the silver bromide, the same inventors proposed to color-sensitize the emulsion (Eng. P. 24290/04; Ger. P. 158517).

Some extensions to the chemistry of the bleach solution were made by the Neue Photographische Gesellschaft (Ger. P. 196962), the Plastographische Gesellschaft Pietzner & Co. (Ger. P. 117530, 196769; Fr. P. 363584), J. Mezaros (Fr. P. 352815), and F. E. Ives (U.S.P. 1186000; Eng. P. 15823/13), who acidulated the bleach solution, and added bromide to it. The addition of these components made the action visible, for a simultaneous bleaching of the silver image took place. As was pointed out in the chapter on carbon and carbro, the presence of some silver ion precipitant is essential for the gelatin tanning to take place. These few references do not by any means exhaust the list of people who patented some slight inconsequential changes in the bleach solution. The historically minded reader is referred to the patent files for a fuller discussion.

The most popular procedure utilizing the tanning bleach principle is the one Eastman introduced in the middle nineteen-thirties, under the name of Wash-Off Relief. It is an excellent process, capable of giving very good results. It deserves, therefore, some detailed consideration. A yellow-dyed positive emulsion is used for the matrix material. To control the depth to which the printing light can go, it was advised to print through a C5 filter. Development was to be in DK-50, which is a modified borax formula

Metol	2.5 parts
Sulphite	25.0 parts
Hydroquinone	2.5 parts
Kodalk	10.0 parts
Potassium bromide	0.5 part
Water	1000 parts

Kodalk could be replaced by an equal quantity of sodium metaborate, its equivalent. The recommended time of development was five minutes at 65 F. After a wash, which must be quite thorough, the matrix is bleached in acid dichromate. This is compounded from two stock solutions.

A. Ammonium dichromate	20 parts
Sulphuric acid	7.2 parts
Water	1000 parts
B. Sodium chloride (Common table salt)	45 parts
Water	1000 parts

In compounding solution *A* the ammonium dichromate should first be dissolved in the water, which should be cold. The sulphuric acid is then added cautiously. Never add the solution to sulphuric acid.

The working bath is made by mixing equal parts of *A* and *B*, then diluting with six parts of water. After the matrix has been in the bleach for one minute, it is safe to turn on the white light. The time of treatment should be sufficient to cause the complete disappearance of the silver image, plus one minute. When finished, the relief image is developed in hot water at a temperature of 120 F. The etch is finished when no more cloudy wash water runs off the matrix. As a rule from three to five minutes treatment should be sufficient. If a continuous supply of hot water is not available, four or five changes, each one minute in duration, could be used.

At this point, the gelatin relief is very delicate. It is necessary to set it. This can be done by placing it in cold water, then fixing in alum hypo. After a final wash, the matrix is dried. An alternative method is to set the gelatin in cold alcohol. This dehydrates and toughens the image directly. After allowing the alochol to dry, the matrix could be fixed, washed, and dried again.

This delicacy of image is the one weak point of the entire processing. To overcome it, the writer changed the developer somewhat. The sulphite was reduced to a bare minimum consistent with fair keeping qualities, and pyro was added. Obviously this is capable of considerable variation, and it becomes possible to go all the way from a non-tanned image to a completely tanned one. A successful formula was

Pyro	2 parts
Sodium sulphite	15 parts
Hydroquinone	8 parts
Sodium carbonate	10 parts
Potassium bromide	2 parts
Water	1000 parts

The addition of copper sulphate to the bleach solution likewise adds toughness to the image. This was a feature of the Brewster procedure for a long time. The bromoil technicians were the first to use copper salts in the bleach baths. Their need was for an image that approximated the dichromate-light-reduced images in toughness. The same is true for the technician who desires to make multiple transfers from the same matrix. It was this need that led Technicolor to the use of a pyro matrix, which is second only to carbon for toughness. Next in line comes carbro, then finally Wash-Off Relief using a tanning bleach.

The last general procedure for the preparation of matrices softens the gelatin in situ with a silver image. This process is based upon a finding by Liesegang (*Phot. Archiv.*, Vol. 32 (1897), p. 161). When a gelatin layer containing a silver image is placed in a bath containing ammonium persulphate, the gelatin immediately surrounding the silver becomes soft, or with prolonged treatment, dissolves away. A year later Andresen (Ger. P. 103516) suggested that hydrogen peroxide produced the same effect, especially if hydrochloric acid were present. The bath used by Andresen contained three per cent peroxide and two per cent hydrochloric acid. Apparently in ignorance of this work, Houzel published a procedure for the making of carbon prints by this technique (*Phot. Woch.*, Vol. 48 (1902), p. 386). He attempted to remove dichroic fog from some prints, so he placed them overnight in a solution of hydrogen peroxide. The next morning he discovered that all the parts containing silver were etched away or dissolved. He then covered the whole surface of the etched print with ink, and dried it. A warm water bath now dissolved the gelatin relief, carrying with it what ink was on top. This left a correct image consisting of ink. Koppmann patented a variation of this in 1924 (Ger. P. 400663).

The application to the making of matrices was suggested by E. Coustet (*Mon. Phot.*, Vol. 42 (1903), p. 251). He developed the silver image in ferrous oxalate, then treated the negative with persulphate solution until complete bleaching resulted. The softened gelatin he removed by gentle friction — a not very satisfactory procedure. The relief was then tanned by treatment with alum, and dried, after which it was dyed and transferred. Mr. Coustet marketed a bleach solution under the name of "Bioxhydro," which was very suggestive of hydrogen peroxide. Valenta identified the active ingredient of the bath to be peroxide (Wall, "History of Three-Color Photography," p. 357). The Coustet technique was applied by H. S. Schnauss (*Phot. Rund.*, Vol. 13 (1903), p. 282), directly to the separation negatives, thus obviating the necessity of making positives from which to print. But this meant that the original was destroyed, a cardinal sin in photography.

The chemistry of the etch solution was studied by Lüppo-Cramer (*Phot. Korr.*, Vol. 48 (1911), pp. 466, 608). He found that silver acted catalytically, and that presence of silver ions in the solution retarded the reaction with gelatin. This explains the necessity for the presence of halogen ions in the bath, for these would precipitate the silver ions, thus removing them from the solution as fast as they are formed. E. J. Wall ("History of Three-Color Photography," p. 357) and Belin and Drouillard (Fr. P. 423150;

Ger. P. 230386) discovered, independently of each other, that the addition of copper salts also aided the reaction. Wall suggested ("Practical Color Photography," p. 91)

Hydrogen peroxide	30 parts
Copper sulphate	20 parts
Nitric acid	5 parts
Potassium bromide	0.5 part
Water to	1000 parts

He was very partial to the procedure. This was because the bleach bath operated at room temperature, obviating the need of a hot-water etch, and removing the danger of bad registry due to unequal stretch of the matrix material. The bad feature of the process is that it is a reversal. The final image is the complement rather than the direct result of the initial exposure.

It required no stroke of genius to remedy this trouble. Riebensahm and Posseldt made the necessary variation in their application of the technique to pigmented emulsions (Ger. P. 144554). After the exposed paper was developed, the silver image was removed by well-known means, such as treatment with acid dichromate or acid permanganate. The residual silver bromide was then exposed and developed completely, and finally treated with the peroxide bath. This removed the gelatin and silver formed in the second development. A similar procedure was again disclosed a full generation later by W. Frankenburger and G. Rössler (U.S.P. 2178338). The application to the making of matrices suitable for motion pictures, was made by L. E. Taylor (U.S.P. 1518945, 1518946).

To be of use, the matrix must be capable of staining with a dye that will later transfer to another gelatin surface brought in contact with it. By the very nature of its formation, the gelatin in the matrix is highly tanned. The gelatin in the blank which is to receive the dye transfer, is only partially tanned. In this differential most probably lies the reason for the movement of the dye from matrix to blank. For a dye to stain gelatin, it must be a member of the class known as acid dyes. The dye anion forms a union with gelatin, especially in the presence of weak acids. Too low a pH, indicative of high acid content, will usually precipitate the dye. An alkaline solution will not fix the dye to the gelatin. These facts are utilized to control the extent to which the matrix is stained. As pointed out above, this knowledge comes to us mainly from the disclosures of F. E. Ives. In Eastman's Wash-Off Relief system, the dyes are sold in powder form. It is quite possible that the powders have been cut with buffering agents, but no definite knowedge of this has ever been published.

The dye baths are prepared by dissolving the powder in distilled water. The strength of the dye bath can be judged only from the fact that one ounce of the powder will make 170 fluid ounces of solution. This is in the ratio of 25 to 5000, or one to 200. The contrast of the dye image can be controlled by the addition of acetic acid. With the Eastman dyes, a saturation point is reached when 30 cc of 28 per cent acetic acid has been added to 500 cc of dye solution. Beyond this acidity no further increase in dye absorption can be noted. It is well not to juggle the acid strength of the bath each time a matrix is to be dyed. A better plan would be to have three or four baths ready, which differ from each other only in the acid content. If a dyed matrix is seen to be too flat, it can be discharged by washing in a one per cent solution of ammonia, after which it is washed in plain water to remove the ammonia. The matrix can finally be re-dyed in a bath containing more acid than the first. It is of course desirable to know the relationship between contrast and acid content. This can be determined by measuring a dyed wedge through a complementary filter.

This method of control of image contrast may be suitable for the technician who makes a single print, and so can spend considerable time in manipulations. However, the commercial laboratory cannot do this. It is not surprising, therefore, to note that Technicolor loads its formulas with acetic acid (U.S.P. 1807805, 1807809, 1900140; Eng. P. 270279). By this means a variable is fixed, and it can no longer plague the technician with possible irregularities. A two-color system utilized the following baths:

Red

Fast red S, 3% solution	10.0 parts
Acid magenta BN, 6% solution	4.5 parts
Metanil yellow	0.03 part
Acetic acid	0.9 part
Water to	18 parts

Green

Pontacyl green SN, 4½% solution	6 parts
Metanil yellow	0.022 part
Acetic acid	0.6 part
Water to	18 parts

The stock dye solutions were purified by a special treatment with egg albumen (U.S.P. 1735142; Eng. P. 270279). The dye was dissolved in warm water. To this was added egg albumen, after which the solution was brought to a boil. At this point 50 cc of glacial acetic acid per liter of solution was added, the solution brought to a boil to coagulate the albumen, cooled, and filtered. The colloid took down with itself the heavy metal salts and other impurities which had a deleterious effect upon the matrix.

For three colors the following may serve (U.S.P. 1900140):

Yellow

Anthracene yellow GR or Sulphone yellow R	0.090 part
Acetic acid	0.45 part
Water to	18 parts

Magenta	
Acid magenta 2B, 6% solution	4.0 parts
Acid magenta BN, 6% solution	0.3 part
Fast red S, 3% solution	1.5 parts
Acetic acid	0.6 part
Water to	18 parts
Cyan	
Pontacyl green SN, 4½% solution	5.7 parts
Fast acid green B, 3% solution	2.8 parts
Acetic acid	0.6 part
Water to	18 parts

It was mentioned above that the art of contrast control by means of acid could be traced to F. E. Ives. This is disclosed in his English patent 15823/13. His recommendations were as follows:

Cyan	
Alizarin blue AS	1 part
Citric acid	1 part
Potassium citrate	1–3 parts
Water to	1000 parts
Magenta	
Alizarin rubinol 3g	1 part
Citric acid	1 part
Potassium citrate	1–3 parts
Water to	1000 parts
Yellow	
Sulphone yellow R	1 part
Citric acid	1 part
Potassium citrate	1–3 parts
Water to	1000 parts

This disclosure contained several other features now standard practice in Wash-Off Relief technique. The dyed matrices were rinsed with strong (ten per cent) acetic acid solution. This prevented or minimized the diffusion of the dye into the wash water. By this means it became possible to remove only the dye solution adhering to the surface of the matrix. It also enabled the technician to judge the balance more accurately, for the dyed matrices could be superimposed on the bottom of a white tray containing ten per cent acetic acid solution. After proper balance has been achieved, the matrices could be left in the acid until needed for transfer. This removes the danger of drying.

A survey of the textile dyes that could serve for imbibition purposes was made by J. S. Friedman (*Am. Phot.*, Vol. 34 (1940), p. 531). The dyes were prepared as a two per cent solution in five per cent acetic acid. A step-wedge matrix was stained and transferred upon a fixed-out piece of film. Since these tests were made with a view to the preparation of transparencies, the transfer density was much heavier than would be required for paper prints. This decrease could be achieved either by the use of much more dilute dye baths, or by the preparation of much thinner matrices. The following dyes appear to be interesting possibilities for a three-color process:

Magentas

Pontacyl light red 4BL
Pontacyl carmine 2g
Violamine RR
Pontacyl carmine 2B
Alizarin rubinol R
Acid magenta 2B (conc)
Fast fuchsine g
Fast crimson 6BL

Cyans

Pontacyl green S
Pontacyl green SN
Alphazurine 2g
Wool green B
Patent blue (conc)

Yellows

Pontacyl light yellow 3g
Pontamine fast yellow NN
Pontamine yellow CH (conc)
Tartrazine O
Fast wool yellow 3gL
Azo yellow
Aceko fast light yellow Ex

To achieve a better control in the multiple staining of matrices, the Uvachrome Company controlled the dispersity of the dye particles in the staining bath (Eng. P. 333392). This was accomplished by fractionating the solutions by means of dialysis, ultra filtration, etc. Technicolor found that when a matrix has been used for many transfers, the dyes begin to build up, especially in the shadows. This causes an appreciable loss in the tone scale which the matrix could cover. To eliminate this trouble, the matrix was given a bath after transfer, in a two per cent ammonia-alcohol-water solution (Eng. P. 322173).

It was mentioned above that F. E. Ives suggested as far back as 1913 that the gelatin surface receiving the transfer be treated to aid it in absorbing and retaining the dye. Technicolor found that it was very desirable to control the ability of gelatin to imbibe dyes, and developed a system of determining the capacity of the blank to do this. The film or blank was dipped into a specially compounded green dye bath, at a temperature of 18 C, for a period of fifteen seconds, after which it was rinsed in water at the same temperature for a like period and dried. A gelatin that was suitable for use in their process had a dye absorption between two limiting values. These values were determined by trial and error. Every piece of film that was to be used was tested in this manner, and all film was sorted into a number of classifications. It was usually found that when the dye absorption was too large, the definition of the image suffered. When it was too low, the contrast suffered. Hence the two limits. Contrasty matrices could be saved by transferring them upon a hard blank; soft matrices upon a soft blank, that is, one which had a high index of dye absorption. This was determined by reading the dyed test strip in a densitometer through a red filter.

Before the advent of sound-on-film, it was possible for Technicolor to make the blank specially for their purposes. If the gelatin is left untanned, it will be able to absorb the dyes with extreme ease, but the definition will be extremely poor, since the transferred dye will diffuse in the blank almost as well as it diffuses out of the matrix. Tanning of the gelatin with chromium naturally suggested itself immediately. F. C. Atwood suggested that a dichromated gelatin be cast upon the base, and the film be subjected to SO_2 fumes, which would reduce the dichromate to chromic salts (U.S.P. 1801478). J. F. Kienninger suggested that the dichromated film be bathed with sulphites (U.S.P. 1851166; Eng. P. 288146). Mrs. B. S. Tuttle discovered that for best results the dichromate should be acidified with acetic acid, and that the reduction should be accomplished by the gelatin itself, at an elevated temperature (U.S.P. 1939738; Eng. P. 270280). When sound-on-film was introduced, Technicolor printed and developed the sound as a silver track. The remaining silver halide was fixed, the film then washed thoroughly and treated finally with a five per cent basic chrome-alum solution. By maintaining rigid controls all along the line, it was possible to obtain a blank with a surprisingly uniform dye absorption index. The procedure for accomplishing this was outlined by L. T. Troland in his English patent 344026 (U.S.P. 2085877), and also by Mrs. Tuttle (U.S.P. 2079470; Eng. P. 484411).

Eastman recommends treatment of the blank with aluminum sulphate or potassium alum. Almost any photographic paper could be used except those with rough surfaces. The best papers are the mat or semi-mat type. These must first of all be fixed out in a fresh alum-hypo fixing bath such as Eastman formula F–5:

Hypo	240 parts
Sodium sulphite, desiccated	15 parts
Acetic acid, 28%	47½ parts
Boric acid	7½ parts
Potassium alum	15 parts
Water to	1000 parts

The paper is then washed thoroughly, after which it can be treated with the special mordanting baths. The first of these is prepared by the slow addition of a solution which contains 40 parts of desiccated sodium carbonate in 500 parts of water, to another which contains 200 parts of aluminum sulphate in 1000 parts of water. When the addition is made, a white precipitate is first formed, but this redissolves upon stirring. When all the carbonate has been added, a clear solution should result. If there is any precipitate left it should be removed by filtration. The paper is bathed in this solution for five minutes, after which it is washed for five minutes. It is then bathed in five per cent sodium acetate for five minutes, and followed by another wash. If the paper is to be used immediately, it need not be dried; but if it is dried and stored away, it should be soaked in water for a period of at least five minutes.

When the blank was made from a fixed-out film or bromide, it was found that a freshly prepared sheet acted differently from one that had aged more than twenty-four hours. It appears that the action of alum or chromium on the gelatin continues for a while. In a typical case, where the fixed-out film was prepared by giving a final bath in seven per cent titrated chrome alum, the following results were obtained:

Age of Blank	*Dye Absorption Index*
1 hour	66.0
6 hours	64.0
20 hours	61.0
44 hours	59.1
70 hours	59.0

The age of the blank was calculated from the time the film came out of the drier to the time the dye-absorption test was made. This was done by measuring the amount of dye absorbed by the film in fifteen seconds, followed by a rinse in water. The index is the reading on a Martens densitometer, so that it represents degrees. These are related to density by the equation $\log \tan^2 \theta =$ density, where θ is the angle determined in the Martens densitometer. The dye used was a green, and the reading was made through a red filter. Upon conversion into densities, the dye absorbed by the same material, differing only in age, was the following.

Age in Hours	*Density*
1	0.70
6	0.62
20	0.52
44	0.44
70	0.44

From this it is seen that in the first day the ability of the blank to absorb dye dropped rather fast. A slow drop continued to take place for the next twelve to twenty-four hours, after which constancy was obtained.

It is not at all certain that there is any reaction between the dyes and the chrome or other alums, during staining. It is possible to replace the alum with formaldehyde, and for best results, the formaldehyde bath should contain some urea to control the swelling factor, and some acid. The fixed and washed film was bathed for five minutes in

Formaldehyde 40% solution	25 parts
Urea	10 parts
Acetic acid	5 parts
Water	1000 parts

It was dried immediately after treatment. The results were as follows:

Age in Hours	*Dye Absorption Index*	*Density*
1	62.3	0.558
3	62.2	0.554
16	62.0	0.548
40	61.5	0.530
100	61.4	0.526
200	61.2	0.518

Now it is seen that the blank is practically at equilibrium from the first hour, and that the change over almost two weeks is negligible. These variations must be kept in mind when large amounts of transfer paper are prepared at one time and stored away for future use.

Instead of transferring dyes, it has been proposed by F. Lierg to transfer a component, which would later be converted into color (U.S.P. 2036945). Thus a nickel salt could be transferred to a blank, and this treated with dimethyl-glyoxime to form the normal magenta obtained by chemical toning. Or a ferrous salt could be transferred, and the transfer treated with ferricyanide. The variations to this technique are manifold, and the many variations have been duly patented. G. Szasz transferred a stabilized diazonium salt. This could be converted into the dye by a treatment with the proper coupling agent (Eng. P. 451190; cf. also 341154 and 384312). Brewster patented the transfer of a silver or copper salt which he later converted into the iodide. This last is finally treated with a basic dye which becomes mordanted to the silver or copper iodide hydrosol (U.S.P. 2070222).

The direct transfer of the extremely brilliant basic dyes was first proposed by R. von Arx (U.S.P. 1643529; Eng. P. 245163). The general theory of this technique is that the matrix is treated with some solution such as silver iodide which will cause it to fix the dye in proportion to the image density. The dyed matrix is then brought into contact with the blank. This is made to contain a much stronger dye mordant than is present in the matrix. Under these conditions the dye will transfer from the relatively weak mordant in the matrix to the strong mordant in the blank. There are several advantages to this procedure. The images are sharper, since no diffusion takes place after the dye becomes fixed in the blank. The dyes are more brilliant, since the basic dyes are the finest available when only shade, brilliance, and purity are considered. The disadvantages are the lack of stability of the dye images, and the long times required to effect transfer.

This procedure necessarily requires different matrix material from the others. F. Lierg did quite a bit of work along these lines (U.S.P. 2054261; 2073212; Eng. P. 353819, 344365). The matrix emulsion was made to contain substances which would fix the dyes loosely. Basic dyes could be fixed by alkali, acid dyes by acids. Or the matrix could contain albumen which would have a high affinity for some dyes. The blank would then contain substances that would release the dye, and other substances that would fix the dye once it transfers to the blank. The agent that releases the dye must be capable of diffusion out of the blank and into the matrix. The agent that fixes the dye once it transfers, must be non-diffusing. It might be stated that it was in these experiments that Mr. Lierg discovered how to make substances non-diffusible, which he later applied to monopacks.

The blank must be specially prepared, and a number of experimenters have tackled this phase of the problem. F. J. Tritton, in a general patent dealing with imbibition (Eng. P. 330199) describes the preparation of the blank. It is made to contain magnesium salts and is tanned with formaldehyde. It is also possible to use aluminum hydroxide, zinc oxide, ferric hydroxide, metastannic acid, antimony or bismuth oxychloride, lead or barium sulphate, lead molybdate, etc. A typical gelatin casting solution is

Gelatin	20 parts
Water	150 parts
Magnesium sulphate, 20% solution	50 parts
Ammonia	5.7 parts
Saponin	6.0 parts
Formaldehyde, 2½% solution	1 part

The blank is suitable to receive both acid and basic dyes, hence could be used in all imbibition procedures. R. Gschöpf (Eng. P. 430823) suggested that the gelatin contain the complex acid such as phospho-tungstic, silico tungstic or antimony tungstic acids. These are excellent pigmentary agents for basic dyes, and are usèd in that capacity by the pigment manufacturer. The same inventor, in conjunction with K. Pokorny disclosed the use of organic acids like oxy naphthoic acids (U.S.P. 2124371). The use of silico tungstic acid was also disclosed by A. Jasmatzi (Eng. P. 481822) and by L. O. A. Pollak (Eng. P. 504790). In the last disclosure, a casting solution was prepared by dissolving 30 parts of a hard (tanned) gelatin in 500 parts of warm water. At a temperature between 60 and 70 C there was added 15 parts of silico-tungstic acid dissolved in 100 parts of water. A white gummy precipitate was formed. This was washed thoroughly in cold water, dispersed in hot water, and cast upon a paper base.