

GASPARCOLOR AND THE SILVER-DYE-
BLEACH PROCESS

FINELY divided silver can act as a catalyst. It has been proposed to utilize this property in the destruction or the formation of dyes, in situ with the image. These efforts culminated in the successful Gasparcolor process, although as utilized by Dr. Gaspar it is doubtful if a truly catalyzed reaction is involved. There is little doubt, however, but that the historical development proceeded in that manner. Probably the first use of the catalytic property of silver was in 1889, when E. Howard Farmer disclosed the action of a silver image upon strong dichromate solutions (Eng. P. 17773/89). When a plate or film, containing a silver image, is immersed in a 20 per cent solution of ammonium, sodium, or potassium dichromate, the gelatin immediately surrounding the silver grains becomes tanned, the silver itself remaining apparently unaffected. As Farmer described the action, the dichromate and gelatin react under the influence of the catalyst silver, so that chromium salts are formed. These combine with the gelatin to form a tanned form of that colloid. The action is extremely rapid. We will discuss this reaction in greater detail in a later chapter, when the subject of Wash-Off Relief is taken up.

In 1897 R. E. Liesegang disclosed another somewhat similar action, this time with ammonium persulphate (*Phot. Archiv.*, Vol. 32 (1897), p. 161), but now instead of forming a tanned image, there is formed an image of soft gelatin. The action of persulphate was to soften the gelatin in situ with the silver. An improvement in this procedure was introduced the following year by M. Andresen (Ger. P. 103516). He found that hydrogen peroxide, especially in the presence of the halogen acids, greatly accelerated this action. The further development of both this and the Farmer disclosure, appears to have been restricted to the preparation of matrices, and we will leave until we come to that subject the more detailed discussion of these reactions. Now we are merely interested in the fact that even before the turn of the twentieth century, the catalytic action of the metallic image was already noted.

A further extension, one that is closer to the form of the reaction in which our present interest lies, was made about 1903 by Ostwald and Gros (*Jahrbuch*, Vol. 17 (1903), p. 519), in a paper describing their "Catatype Process." They pointed out that the oxidation of pyro by potassium bromate was tremendously accelerated by platinum. If a sheet of paper, sensitized with a mixture of pyro and potassium bromate be squeezed to a platinum print,

and the two left in contact from 45 to 60 minutes, a brown image will be formed in the paper, corresponding to the platinum image in the print. This reaction can be further catalyzed by copper sulphate. In the same paper they note also that if a silver or platinum image be flooded with peroxide, nascent oxygen will be liberated in situ with the metallic image, thus indicating a destruction of the peroxide at these points. By this means it becomes possible to form a negative image composed of peroxide which can be made to undergo other reactions. It is interesting to note that this scheme, although not proposed for the formation of color images, could be utilized for that purpose. If peroxide is destroyed in situ with the silver image, then oxygen must be released at these points, and this oxygen could be utilized to form a color image by its action upon leuco dye bases, leuco ester salts of the vat dyes, or upon mixtures of paraphenylenediamine developers and coupling agents (cf. chapters dealing with Toning and Color Development processes). The same is true with the action of bromic acid or bromates.

Shortly after this article appeared, Dr. Karl Schinzel proposed a complete process for the making of color prints, utilizing the catalytic destruction of dyes by the oxygen released from peroxide in contact with a silver image (*Brit. J. Phot.*, Vol. 52 (1905), p. 608; *Aust. P.* 42478; *Phot. Woch.*, 1905). The disclosure is important from another point of view. It is one of the first patents which contains a complete description of a monopack. A plate was coated with three emulsion layers, one on top of the other, and separated from each other by plain gelatin layers. The entire group formed a single inseparable unit. Each emulsion layer was sensitized to but a single primary color, and was dyed in mass to a color complementary to its sensitivity. Thus the top layer, sensitive to the blue rays, would be dyed yellow. The central layer, sensitive to the red, would be dyed cyan. The bottom layer, sensitized to the green, would be dyed magenta. Therefore each layer completely removed the light to which it was specially sensitized, making for complete and accurate color analysis. The dyes that were used were stable to the action of water, alkaline developers, and fixing baths, so that after exposure, development, fixation, and washing they would remain intact in the gelatin layers, together with a silver image depicting the densities due to the individual primaries. The final step was to immerse the plate in a peroxide solution. Where this substance came in contact with the silver, oxygen was released. This bleached the dye immediately about the silver. Since the amount of oxygen released depended upon the amount of the silver, the destruction of the dye followed the image density. Where there was a heavy deposit of silver, there most of the dye became bleached. Highlights in the original were recorded, therefore, as highlights in the dye image. The process gave a direct positive.

As long as one did not examine the procedure too closely, it was an excellent solution to the problem of making color prints, especially from other color transparencies such as Autochromes, etc. But the practice left much to be

desired. At the time the idea was proposed, the available dyes did not have the stability to peroxide that the procedure called for, so that it was extremely difficult to prevent the bleaching of the dyes at non-image portions of the layers, a fact pointed out by R. Neuhauss almost as soon as the idea was proposed (*Phot. Rund.*, Vol. 19 (1905), p. 239). This was admitted by Schinzel in a second paper in which he discussed several other highly theoretical procedures (*Chem. Ztg.*, Vol. 32 (1908), p. 665). Ideas along these lines were also advanced by F. Sforza (*Phot. Conf.*, Vol. 4 (1909), pp. 23, 101) and R. Luther (*Phot. Rund.*, Vol. 25 (1911), p. 1). But the procedures for the isolation of the dye image differed from that of Schinzel. Sforza, for instance, converted the silver into a dye mordant, thus fixing the dye in the form of a silver-salt complex. Upon treatment with hypo, this dissolved out, leaving a positive image behind. Of course all of the ideas expressed were hypothetical, as no reduction to practice was indicated by any of the gentlemen. When the Schinzel disclosure was cited as a prior art against Dr. Troland, he answered that Schinzel never reduced his art to practice, and since the Troland monopack patent (cf. chapter on Monopacks) was issued, it may be inferred that this argument was acceptable. But to Schinzel must go the credit for being the first person to suggest the catalytic destruction of a dye for the formation of a color print. This suggestion culminated in the successful Gasparcolor process.

In the Schinzel scheme, the dye was apparently destroyed by oxidation. The reverse reaction, dye destruction by reduction, was outlined by Christensen in 1918 (U.S.P. 1517049; Eng. P. 133034; Ger. P. 327591; *Jahrbuch*, Vol. 29 (1920), p. 164). He found that certain dyes would be destroyed by hydrosulphite, at room temperature, only in the presence of finely divided silver. After exposure, development and fixation, a film may be dyed with any of the following dyes:

Oxamin echt rosa	Diamine fast red F
Aurophenine	Benzoazurine G
Dianil pure blue	Rosophenine SG
Congo pure blue	

After being uniformly dyed, the film was treated with a solution containing from one to three per cent of sodium hydrosulphite or stannous chloride. The dye was bleached only in situ with the silver image, and to an extent depending upon the density of the image. It is possible to add the dye to the emulsion, or to bathe the film immediately after the exposure. In this event, development and dye-bleaching could take place simultaneously by treating with

Sodium hydrosulphite	20 parts
Potassium bromide	20 parts
Water to	1000 parts

The silver could be removed by treatment with Farmer's reducer. A scheme such as this could be utilized with advantage in those processes where three

layers containing the color part-images are superimposed to form the complete color print. The Defender Chromatone stripping paper, or some similar material, could be used.

Almost contemporary with the Christensen disclosure was the one made by George Pascal Joseph Schweitzer (*Fr. P.* 476213). He suggested that the silver image be converted into lead chromate, after which the film was dyed in mass. When this was washed with acid, it was found that chromic acid was released, which destroyed the dye in its immediate vicinity. By this means a direct positive was obtained — highlights in the original were reproduced as highlights in the colored image. Suitable dyes were tartrazine, aniline green, orchil, safranin, methyl blue, and methyl violet. In a later disclosure (*Eng. P.* 249530) he extended the scope of the reaction. The dye could be included in the emulsion. Three layers could be coated one on top of the other, in the form of a Schinzel monopack. After exposure, development and fixation, there would be obtained a silver image in each of the dyed layers. A final treatment must be given in a bath such as

Sodium bromate	15 parts
Sulphuric acid (concentrated)	10-20 parts
Water to	200-300 parts

In this bath the dye becomes destroyed in situ with the silver image, which acts upon bromic acid to decompose it, probably releasing nascent oxygen.

In another modification, it becomes possible to effect just the opposite result. The monopack is exposed and developed, but not fixed. Upon treatment with

Iodic acid	1 part
Sulphuric acid (concentrated)	3-5 parts
Alcoholic iodine, 25%	10-15 drops
Water to	200 parts

the dye becomes destroyed only in those places where the silver bromide exists. It is left undisturbed in situ with the silver image. A black-and-white positive becomes converted into a color positive. There is some advantage to such a procedure, since the amount of dye that remains at each point depends upon the original silver image. The dye is destroyed at all other places.

In German patent 396485 R. Luther and K. von Holleben made a slight variation from the above general procedure. The dye that was to form the final image was incorporated in the emulsion. After exposure, development and fixation, the silver image was converted into vanadyl ferrocyanide. The vanadyl ion acted as an oxygen carrier in the next step, which consisted in treating the dyed layer with chromic or hydrobromic acid. The dye was destroyed in situ with the ferrocyanide image. To make positives, the silver image should be a negative, so that printing was to be done from positives. This makes it convenient as a duplicating material, especially when Kodachrome transparencies are to be duplicated. The one disadvantage is that the image itself is what remains, after exposure and development. This means

that absolute uniformity in coating is required. But this is a problem that had to be solved to a high degree of perfection during the last two decades, since the same problem exists in all reversal processes. Years later Dr. Gaspar revived the use of vanadium ions as a catalyst in a different type of oxidation, this time in the oxidation of leuco ethers, esters, and ester salts of the vat dyes (cf. chapters on Toning).

In 1921, Mr. Crabtree of the Eastman Kodak Laboratories disclosed another procedure by which dyes were destroyed by reduction, in situ with a silver image (Communication No. 97, Eastman Kodak Laboratories; *Photo Era*, 1921). Dyes that were easily reduced to the leuco form, such as methylene blue, methylene green, fuchsine, etc., were bleached in situ with a silver image, if the dyed image layer were treated with

Hypo	5 parts
Acid hardener	2½ parts
Water to	100 parts

The acid hardener is made by dissolving 56 parts of alum, and a like amount of sodium sulphite, in 1000 parts of 10 per cent acetic acid. The time of treatment is from three to five minutes, after which the layer should be thoroughly washed so that the leuco dye bases are completely removed. If this is not done in a thorough manner, the unremoved leuco salts will reform the dye when the plate or film is treated with Farmer's reducer to remove the silver. It was also suggested that the leuco derivatives could be mordanted to the gelatin by some means that is not effective upon the dye. In that case it becomes possible to wash the film free of the unreacted dye, then treat it with ferricyanide to regenerate the color. By this means the final dye image is directly related to the silver image, and not to what is left behind after the silver image has been removed. This scheme is really worthy of further study. For one thing, an attempt should be made to expend the reaction to those colors which form stable leuco derivatives that are soluble in alkali and so can be washed out readily. As a rule, strong reducing agents, such as alkaline hydrosulphite, zinc-acid, zinc-alkali, etc., are required for the reduction. But possibly the catalytic action of the silver image would allow milder agents.

After Crabtree, the idea appears to have become dormant until Dr. Bela Gaspar tackled it in a thorough and painstaking manner. After developing the original reaction (the reduction of dyes in situ with a silver or silver salt image), to a usable state, Dr. Gaspar made a thorough study of the many other secondary variables whose previous non-uniformity was the stumbling block upon which the commercial application tripped. Problem by problem, Dr. Gaspar overcame these difficulties, until he was ready to launch a full utilization of the procedure to make prints in color from color transparencies.

There are at least four different phases to the successful application of the silver-dye-bleach processes. First of all, the fundamental reaction, the destruction of the dye in direct proportion to the silver image, must be made

completely foolproof and applicable over a fairly wide range of variations in solution composition. Motion-picture work requires millions of feet to be processed continuously, hence means must be found to guarantee the life of the solutions, so that results at the head and tail ends of a run will be uniform. The action must be fairly rapid, hence as great a differential as possible must be maintained in the reactivity of the solution upon dyes in the presence and in the absence of silver.

A second problem is to diffuse the color uniformly through the gelatin layer. If some color is heavier at one spot, then regardless of how proportional the reaction may be, the result will be non-uniform, since there will be a disproportionate amount of dye left in the more concentrated regions. The dye must be very finely dispersed in the gelatin, otherwise the resultant image will be coarse and grainy. It must be remembered that the projected motion-picture image represents an enlargement of more than four hundred diameters, especially in the larger theatres where a forty-foot screen is used. The dye must be thoroughly localized and have either no solubility, or no mobility in the solutions used in processing. This problem we have met before, in our discussion of the Agfa version of Kodachrome.

A third problem relates to the proper construction of the monopak layer. The original scheme formulated by Schinzel was to dye each layer the exact complementary to the spectral sensitivity of the layer. Thus the top layer, being blue-sensitive, would be dyed a yellow. One result of such a procedure would be to limit each silver image to a thin upper portion of each layer, making the final dye print flat. For copy material, this type of spectral distribution is unnecessary. Dr. Gaspar has developed a special type of spectral distribution that allows full penetration of the printing light through the entire depth of each layer, and yet does not interfere with other layers. The fourth major problem is the formation of a sound track, equal in quality to the normal black-and-white product. In the present discussion, the Gaspar patents have been classified in accordance with the above system. We will discuss these in detail, since a study of their contents reveals a pattern for the successful solution of intricate and delicate procedures.

Dr. Gaspar's first efforts in color were devoted to mordant and toning processes. These evidently have taught him that the silver in the normal black-and-white image could be made to influence other reactions, such as oxidations or reductions. He quickly realized that either of these could be made to act on dyes to decolorize them. From a realization of this fundamental principle to the utilization of it for the making of color prints, was a very obvious extension.

The chemistry of the reaction is outlined in United States patent 2020775 (Eng. P. 395718, 397158, 397188; Fr. P. 727168). The presence of a non-leuco-forming dyestuff which is uniformly diffused through the gelatin layer, and a metal image are essential for picture formation. The metal image is, of course, the usual silver image produced by exposure, development and

fixation of a normal photographic emulsion. The non-leuco-forming properties limit the selection of the dyes somewhat, but not seriously. Strictly speaking, there is no such thing as a non-leuco-forming dye. What Dr. Gaspar means is that the formation of the leuco form is extremely difficult under normal conditions, so that destruction of the dye rather than leuco formation takes place. The azo dyes fall into this classification, for the formation of hydrazo compounds is extremely difficult. Even when formed they are very unstable. Unlike other leuco dyes, they would probably undergo what chemists term the benzidine or semidine rearrangement. The resultant substituted benzidines, or amino diaryl amines, would be colorless substances capable of being washed out of the emulsion. Dyes of the di and tri phenyl methane series, the indigos, and the other vat colors, all form leuco derivatives, which easily reoxidize to the original dye. Unless the leuco forms are completely removed, the danger is always present that clear and clean-cut images will be difficult to obtain.

The dyes that are suitable for such destruction are of the substantive and acid-azo class, although some basic vats and alizarines are also available. Mentioned specifically are

- Heliotrope BB, No. 321
- Chlor-amine light red 7BL (Sandoz)
- Diamine rose G, No. 119
- Diamine rose BBF (Casella)
- Diamine pure blue FF, No. 424
- Naphthamine light blue 4 B (Kalle & Co.)

The number beside the dye refers to its listing in the fifth edition of Schultz's "Farbstoff-tabellen." The chemical constitution, and the name of the manufacturer, together with all the trade names under which the dye is sold, are given in the tables.

The destruction of the dye can be accomplished either by oxidation or reduction. The actual agents that attack the dyes are formed and act while the finely divided metal forming the image is being acted on by the treating agent. These are divided into two classes, "destructive" and "non-destructive." Reagents which are destructive can attack the dye even in the absence of a silver image, hence are undesirable. Potassium permanganate, bromic acid, and hydrogen peroxide are oxidizing substances in this group. It is interesting to note that Schinzel first proposed to use peroxide, and Schweitzer suggested bromic acid (cf. above). Reducing agents of this class are sodium hydrosulphite (Christensen, cf. above), and stannous chloride. Concentrated solutions of sulphuric acid, and of sodium and potassium hydroxides, acting as solvents for the dyes, can also be classified as destructive, in that they act upon the dye generally. The fact that an accelerated action takes place in the presence of the silver image, brings all of these chemicals into the scope covered by this patent.

Of the other type of agent, there exists quite a variety. These, as has been

pointed out above, act first to form silver salts and products which can reduce the dye, thus destroying it in direct proportion to the intensity of the silver image. Or the silver salts can form complexes which act upon the dye. In either case the reaction follows closely the image density.

Sulphur-containing compounds that can form complex silver salts, are especially useful in this respect. From this point of view, an article by Dr. G. Schwarz, director of the Gevaert Photo-Producten N.V., is of some interest. It is titled "Photographic Silver-Gelatin as a Reagent in Spot Analysis," in *Industrial and Engineering Chemistry* (Vol. 12 (1940), p. 369). It is a well-known fact that when a silver image is immersed in water, then dried, the image loses density in the regions that were wet. Dr. Schwarz found that this decrease in density could be completely negated if the water contained any one of a fairly large series of organic compounds, in concentrations varying in some cases to one part in 100,000. The reaction was recommended as a spot test for the detection of minute quantities of specific materials in solution. Its value lies in the fact that organic chemists have an easy routine to determine whether or not a given reaction mixture still contains undesired material.

To carry out the procedure, a sheet of photographic paper is given an overall exposure to light, then developed to gamma infinity in

Metol	2.0 parts
Hydroquinone	5.0 parts
Sodium sulphite	50.0 parts
Sodium carbonate	50.0 parts
Potassium bromide	1.0 part
Water to	1000 parts

It is fixed in a 20 per cent hypo bath containing 2 per cent of sodium bisulphite, washed, dried, and finally cut into strips. Each of the strips contains a uniform silver density. When a test is to be made, a drop of the solution is placed on the test strip, and is allowed to evaporate to dryness. This should not take long, since most of the water will be absorbed by the gelatin. When dry, the entire strip is placed in hot water, at a temperature between 80 and 90 C. A positive test will be had if the area covered by the drop is appreciably darker than its surroundings. To us the interesting feature of this phenomenon is that all the reagents that give a positive test are those which contain a labile hydrogen, and which can therefore form simple or complex silver salts. This is also a condition that appears to be a requisite for the Gaspar type of dye-bleach solution. Dr. Schwarz details his results with a large number of substances, which by inference, at least, should be usable in Gasparcolor. It is interesting to note that most of the substances mentioned in the Gaspar patents, give positive results.

Some typical solutions that will destroy the dye in situ with a silver image, are the following:

1. Thiourea	10 parts
Citric acid	5 parts
Water	200 parts

A film, dyed diffusely with one of the dyes mentioned above, and containing a silver image, is treated in the above solution. The dye will be destroyed only in the places where a silver image exists. If this be a negative, then a positive dye image remains. Therefore to obtain a positive, the film must be printed through a positive.

2. Semi carbazide	5.0 parts
Sulphuric acid	1.0 part
Water to	100 parts
3. Thio semi-carbazide	5.0 parts
Sulphuric acid	1.0 part
Water to	100 parts

Guanidine and amido-guanidine could replace the agents mentioned above.

4. Sodium sulphide	5.0 parts
Metol	as desired
Water	100 parts
5. Thiodiglycolic acid and sugar	5.0 parts
Water to	100 parts

The chemistry of the reaction was extended in a later patent application, which oddly enough was issued before this one in the United States (U.S.P. 2004625; Eng. P. 419810; Fr. P. addition 43049 to 727168). Here is disclosed the fact that the silver image could be developed and the dye destroyed simultaneously. Ordinarily the developer will not have a sufficient potential to reduce azo dyes, but evidently the catalytic action of the silver makes the reduction possible. Two solutions are given:

1. Amidol	1.0 part
Sodium bisulphite	1.0 part
Sodium sulphite, crystals	8.0 parts
Water	200 parts
and	
2. Sodium hydrosulphite	0.5 part
Potassium bromide	1.0 part
Sodium bisulphite	3.0 parts
Water	100 parts

The second solution differs but slightly from the one offered by Christensen (cf. above). The most important difference, and one which may be an indication of a truer understanding of the fundamental chemistry involved, is the inclusion of sodium bisulphite, making the solution more acid than previously. Dr. Gaspar, in several of his patent specifications states that the fundamental reaction is



This reaction proceeds most generally to the left. The presence of silver ions in the solution would force the reaction to the left, so that under ordinary conditions, the formation of nascent hydrogen by the action of an acid upon metallic silver, would never take place. The need for the presence of an agent which removes silver ions from solution, now becomes evident. When this happens, positive silver is removed as fast as it is formed, thus forcing the reaction to the right. Hydrogen has a very limited solubility in water, so that its concentration is a minor influence. However, this also is removed when an easily reduced dye is present. Hence in Gasparcolor, the conditions are just ripe for forcing the reaction to the right. Nascent hydrogen is an excellent and extremely powerful reducing agent. Since its formation is dependent upon metallic silver, and this is removed during the formation, the production of hydrogen will continue only until the silver is used up.

Amidol is one of the few developing agents which can act even in acid media. But the action under such conditions is extremely slow. Dr. Gaspar suggests, therefore, that the development be started in a normal amidol developer, then finished in an acidified solution. This can be accomplished if a few drops of concentrated hydrochloric acid be added to the original. The amidol could be replaced by pyrogallol, metol, glycin, etc., and HCl can be replaced by other acids. When hydrosulphite is used both as a developer and as a dye destroyer, it must be present in low concentrations, and its activity must be further curbed by the presence of mild acids (strong acids will decompose hydrosulphite) and fairly large concentrations of bromide.

While the formation of nascent hydrogen may be the true explanation when the solutions contain acids and silver-salt complex formers, this cannot be the true explanation in the case just discussed. Here we have only a very mild acidity, and no silver complex formers to remove silver ions from solution. Perhaps the adsorption theory of development provides a clue. According to this theory, the metallic specks forming the latent image act as centers about which the developing ions, such as metol, amidol, etc., adsorb. As a result of this adsorption, the local concentration of the reducing agent is increased to a point where its reducing power becomes sufficiently high to attack the silver bromide, and in the present case, the dye. Since sodium hydrosulphite and peroxide can also act as developers, this explanation must not be overlooked as a possibility in the Schinzel and the Christensen techniques.

In the specifications of this patent, Dr. Gaspar hints at another type of reaction. Instead of having the reaction products between the silver image and the bleach solution act on dyes, they can act upon dyestuff-forming substances, whereby the dyestuff-forming properties become destroyed. The very obvious extension, the reduction of nitro-bodies to amines, is not mentioned in this patent. Under such conditions non-dye-forming compounds become converted to dye-forming substances. One very obvious advantage of this type of reaction is that the intensity of the final image becomes directly proportional to the original silver image, rather than to its complement.

In English patent 397159, several new bleach formulas are given

1. Potassium thiocyanate	3 parts
Citric acid	3 parts
Water to	100 parts
2. Cystein hydrochloride	5 parts
Metol	5 parts
Sulphuric acid	3 parts
3. Phenyl hydrazine hydrochloride	8 parts
Hydrochloric acid	3 parts
Water to	100 parts

All the formulas listed above act upon the dye as reducing agents. In several other disclosures (Eng. P. 397188, 397192), oxidizing solutions that bleach dyes are listed. Here also are included the compositions of the dyed layers. A monopack contains a bottom layer dyed diffusely with diamine pure blue FF, a central layer colored by diamine fast pink G, and a top layer dyed yellow with mordant yellow G. After exposure, it is developed, then treated with either of the following solutions.

1. Sodium chlorate	5 parts
Hydrochloric acid, 20%	5 parts
Water to	75 parts
or	
2. Potassium bromate	5 parts
Sulphuric acid	2 parts
Potassium iodide, 10%	1 part
Water to	100 parts

To this was added either 0.2 part copper sulphate or 0.1 part vanadium chloride to act as a catalyst. In these solutions, the dye becomes destroyed only in situ with the undeveloped silver halide salts, hence the importance of not fixing the emulsion after development. The decomposition of chloric or bromic acid into free chlorine or bromine takes place only in the presence of huge quantities of halide ions in accordance with the reaction



We recall that Mr. Brewster used the equivalent iodide reaction for the formation of his Miller-type silver iodide mordant (cf. chapter on Dye Toning). With bromic acid, a similar action takes place. In the present instance, silver bromide takes the place of NaCl or NaBr, thus localizing the reaction to the immediate vicinity of the insoluble salt. The bleaching action of free halogen is well known.

Another possibility is outlined in these patent specifications. The monopack containing the silver image, can be treated with

Bleaching powder	2 parts
Acetic acid	2 parts
Water to	100 parts

Now the dye destruction will take place in situ with the silver image. In this case it is possible to fix the emulsion before treating it with the bleach solution. These solutions are quite reminiscent of the Schweitzer disclosures, where two baths are given, and the claim made that one solution gives dye destruction in situ with silver, and the other one in situ with the unfixed silver halide.

Instead of converting the silver into a substance which will act on the dye to bleach it, it is possible to convert it into a salt that will react with the bleach and thus prevent its action on the dye (Eng. P. 424563). The dye will in that case be bleached most where the least silver deposit is present. Here again there will be formed a negative dye image.

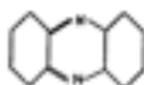
In compounding a bleach it is extremely desirable to have a solution that will act rapidly, for if the time of reaction be unduly prolonged there will be bound to be some action on non-image portions of the layers. In such cases it is usual to look for catalysts. These may serve two purposes. First, they may increase the rate of the general reaction, the reduction of the dye by the agent either present in the solution, or formed by its interaction with silver or silver halide. Secondly, they may increase the differential in the reaction rates between image and non-image portions. In either event the time required for image formation will be considerably decreased. When a thiourea bleach is used, it has been found (Eng. P. 496558) that substances like metol, hydroquinone, etc., are excellent activators, especially in the presence of organic solvents which probably act as solvents for both dye and dye-reduction products. Three solutions are given:

1. Thiourea	19 parts
Hydroquinone	16 parts
Hydrochloric acid (conc.)	2 parts
Ethyl alcohol	30 parts
Water to	100 parts
2. Thiourea	19 parts
Hydroquinone	16 parts
Hydrochloric acid (conc.)	2 parts
Acetone	30 parts
Water to	100 parts
3. Thiourea	16 parts
Metol	3 parts
Sulphuric acid, 30%	1 part
Methyl alcohol	30 parts
Water to	100 parts

It is evident from the examples that only water-miscible solvents are used. In an extension of this patent, it is pointed out that the ortho hydroxy azo dyes, which are insoluble in alkali, are especially useful (Eng. P. 500098).

A more positive type of catalyst is disclosed in English patent 490451 (cf.

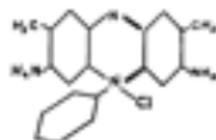
U.S.P. 2183395 for a method of synthesis). This also is to be used with the thiourea type of bleach. The substance phenazine has the structure



Here two benzene groups are bridged together by two amino nitrogens, forming a new six-membered azine ring. If there is present an amino or an oxy group in either of the benzene rings, the result is a dye. Safranin, one of the very first known practical desensitizers, has the structure

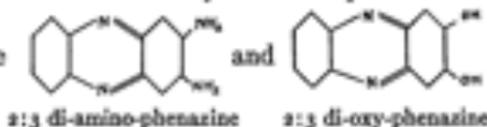


Phenosafranin, another excellent desensitizer, has the structure



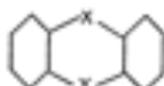
Both of these substances act as catalysts for Gasparcolor. Other phenazines

that can be used are



Also dyes such as Janus blue, methylene blue, and induline scarlet can be used. They also act as desensitizers for the photographic emulsion. Another common property is that they bleach very readily when exposed to light, especially if thiourea and certain thiourea derivatives are present. In the bleached state they are fairly strong reducing agents, being capable of reducing silver nitrate to metallic silver. It may be inferred therefore, that these substances act as hydrogen carriers, becoming reduced readily by the action of the bleach solution, and then reforming the dye by reaction with the non-leuco-forming dye present in the emulsion layer. In general, derivatives of the following type can act in this manner

X can be N , S , or O .
 Y can be N , S , or O .

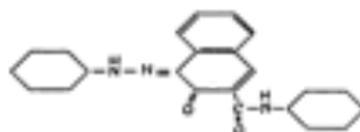


If X and Y are nitrogen, the compounds formed are azines (safranin, phenosafranin, etc.). If X is N , and Y is S the compounds are thiazines (methylene blue). If X is N and Y is O the compounds are oxazines. All the members of these classes of dyes have desensitizing properties, are easily bleached to leuco derivatives by the action of light (an action which is highly catalyzed by thiourea and its derivatives), and they strongly fog photographic emulsions

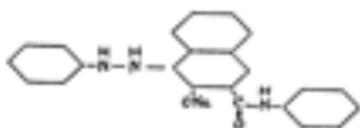
when these are treated with the dyes. In this cycle of common properties may lie the explanation for the catalytic action of the substances in Gaspar-color. Also mentioned are di-methyl-phenyl-benzyl-ammonium chloride (leucotrope O), and quinoline-ethyl-sulphonate.

The second problem which Dr. Gaspar had to solve was to dye the gelatin layer uniformly. The dye must be completely localized, and must not diffuse away from the positions where it is placed. This usually means that the dye must be insoluble in the gelatin and in the solutions into which the gelatin layers might be placed. If this method is adopted for the localization of the dye particles, then another problem arises. The sizes of the dye particles must be made sufficiently fine to insure an image that will not be grainy. One solution would be to colloiddally disperse the dye in gelatin. In order to accomplish this, it is desirable to start with some derivative of the dye which is soluble in water. After solution in the gelatin emulsion, the derivative can be treated so that the original insoluble dye becomes reformed. Under such conditions, especially if gelatin be present, extremely fine dispersion can be made. One method of accomplishing this is to start with a hydrazo compound. These compounds may be considered as leuco azo dyes. By a process of oxidation they become converted into the dye form. As oxidizing agents Dr. Gaspar suggests ferric chloride or nitrous acid (U.S.P. 2041827; Eng. P. 430991; Ger. P. 601572; Fr. P. 766192). In the specifications of this patent, there is suggested that the hydrazo compounds might serve as toning agents. In this case, the silver image must first be converted into lead chromate, which upon treatment with an acid will release chromic acid, a powerful oxidizing agent.

When an azo group is ortho to an hydroxy, as in the dyes of the Naphthol AS series, complete insolubility is achieved even though there is ostensibly present a solubilizing oxy group. This lack of solubility conforms to a hydrazone structure for the dye, thus

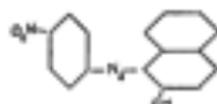


Upon reduction to the hydrazo derivative, there will be formed a true hydroxyl group which would be capable of forming soluble sodium salts



This form will be oxidized very readily by agents such as nitrous acid, ferric chloride, chromic acid, etc., to the insoluble dye. Methods of converting a silver image into an oxidizing agent have been described in the chapter on chemical toning.

The insoluble azo dyes, especially those containing an hydroxy group ortho to the azo, can be solubilized by forming a bisulphite addition compound (U.S.P. 2172307, 2172308; Eng. P. 496559, 498461). Para red, formed by coupling para-nitro-benzene diazonium chloride into beta naphthol



can be converted into a soluble product by the following method. One gram of the dye is refluxed in a solution containing 9 grams of bisulphite, 35 cc of water, 35 cc of alcohol, and 25 cc of chloroform, until the red dye has disappeared. The solvents are partially distilled off, whereupon yellow crystals are precipitated. These can be recrystallized from water.

If the coupling agent is an amine, it is possible to achieve solubility by converting it into the omega sulphonic acid, by treatment with bisulphite-formaldehyde. The omega salt can then be coupled. A dye omega sulphonate will be formed, which is soluble. After dissolution in gelatin, the dye can be precipitated in exceedingly fine state, by treatment with alkali. Instead of the dye, the coupling agent may be made soluble in this manner, and the dye formation carried out after dispersion in gelatin.

A further extension of this idea is contained in United States patent 2178167 (Eng. P. 503873). Nitro or nitroso bodies are dispersed in the gelatin or emulsion layer. After exposure, development, fixation, and washing, the film is treated with sodium hydrosulphite, which will reduce the nitro or nitroso group to an amine, which can then be diazotized and coupled. The resultant dye could finally be bleached in situ with the silver image by treatment with any of the solutions mentioned above. Dr. Gaspar makes an obvious extension of the process in this disclosure. Instead of converting the nitro group generally into an amino body, this conversion is made to take place in situ with the silver image. This can be accomplished if the film is bathed with halogen acids, but a preferred bath is

Water	100 parts
Thiourea	7 parts
Sulphuric acid	1 part
Hydroquinone	6 parts

The time of treatment is ten minutes. After a thorough wash, the film is treated with a solution containing one-half of one per cent of nitrous acid (made by dissolving 5 grams of sodium nitrite in one liter of water), then acidifying with hydrochloric acid. This treatment will convert the amine into a diazonium salt. Upon treatment with an alkaline solution containing a phenol, beta naphthol, or naphthol AS body, a dye will be formed in those places where a silver image existed previously.

In another disclosure (U.S.P. 2071688; Eng. P. 416566, 416660; Fr. P. 747252) Dr. Gaspar describes methods of forming other than azo dyes, in a gelatin medium. Thus various metal salts may be dissolved in the gelatin solution, which by treatment with other salts, will yield pigments. Ferrous salts can be dissolved in the gelatin, and this can later be treated with potassium ferricyanide. By interaction between the two, the cyan pigment Prussian blue is formed in true colloidal dispersion. The ferrous salt may be substituted by lead, and the potassium ferricyanide by potassium dichromate. The net effect will be to form the extremely efficient yellow pigment lead chromate, again in the form of a colloidal dispersion in gelatin. If the emulsion, colored either by lead chromate or Prussian blue, contains a silver image, treatment with one of the baths noted above will cause an imagewise reduction of the pigment to a soluble and colorless form.

It is not important that the diffusely dispersed material be a colored substance. It is possible, for instance, to diffusely disperse zinc ferrocyanide in the emulsion layer. If the latent image be developed with a ferrous oxalate developer, ferric ions will be formed wherever silver is deposited. The ferric ions will immediately react with the ferrocyanide to form Prussian blue. In the specifications, Dr. Gaspar states that zinc ferricyanide must be dispersed in the gelatin. This is an obvious error or misprint. Prussian blue is formed by the interaction of ferric salts with ferrocyanides, and ferric salts will be formed from the action of ferrous oxalate upon the latent image. Hence it is ferrocyanide that must be diffusely dispersed within the gelatin layer.

It is possible to form many organic dyes in a gelatin medium. To form an oxazine dye, resorcin is allowed to act on a nitroso-di-alkyl amine, in the presence of tannins. Many other examples are given. Suitable for this purpose are many of the developable dyes. These are substances that have affinity for the medium in which they are dispersed, so that dyed gelatin is formed. The dyes contain free amino groups which can be diazotized. The dye affinity localizes the diazonium salt, and subsequent coupling forms a new dye that is very substantive.

There are other methods of dyeing gelatin with dyes that will not diffuse out. It is possible, for instance, to start with dyes that are soluble, but which can be precipitated in the gelatin by colorless agents. Nitrogenous organic bases (U.S.P. 2046067, 2075190; Eng. P. 415756, 428158, 516883; Fr. P. 746645, addition 44754 to 746645), such as guanidine, 2 phenyl-4-aminoquinoline, or biguanidines derived from aromatic polyamines, will form insoluble complexes with many dyes, especially if sulphonic acid groups be present. If the precipitation is allowed to take place in gelatin, exceedingly fine or truly colloidal dispersions may be formed.

The dye may be made to react with the salt of a weak acid, and in that manner form a lake (U.S.P. 2107605; Eng. P. 434305). The alkaline earth metals, magnesium, the nitrogenous bases (compounds containing a trivalent nitrogen as part of a heterocyclic ring), etc., form suitable cations to react

with dye-acids. The weak organic acids can serve as anions to unite with dye-bases. The dyes suitable for this procedure need not have any substantive properties for gelatin. It is also possible to form metal complexes of many dyes, complexes sold under the names Neolan or Lanazol dyes (U.S.P. 2055407; Eng. P. 445806; Fr. P. 785665). The metal ions are bound to the dye by means of chelate structures. Such dyes are immobile, and can be used directly. To illustrate the procedure, Dr. Gaspar gives the following example. A silver halide emulsion which contains 0.5 per cent Neolan yellow R, is coated on a film base. On top of this another emulsion layer dyed with 0.5 per cent Neolan pink G is coated. The yellow-dyed layer is green-sensitive, while the pink layer is red-sensitive. After exposure, development, and fixation, dye images can be produced by treatment with a thiocarbamide bleach bath, such as one of the solutions disclosed above. In a three-color process the third layer could be dyed with Neolan green BR. To help disperse the dyes or dye formers in gelatin, wetting agents can be added (Eng. P. 514639). In many cases the dye is soluble in an organic solvent such as alcohol. In that case a coarse dispersion of the dye in gelatin could be treated with alcohol. A fine dispersion will result (U.S.P. 2080041; Eng. P. 458256, 458304).

Instead of adding dyes or color formers to the gelatin, it is possible to add specific precipitants (U.S.P. 2137336; Eng. P. 478735, 480854, 516883). After exposure, the emulsion could be treated with dyes which will combine specifically with each precipitant. It has been found, for instance, that a gelatin layer containing di-phenyl-guanidine acetate will allow the penetration of a one per cent solution of diamine pure blue (Schultz No. 426, 5th edition). The dye will react with the guanidine to form an insoluble complex which, however, will not interfere with the further diffusion of another dye. If the treatment with the blue dye be interrupted and then continued with a solution of xylene light yellow 2G (Schultz No. 22), the yellow will diffuse through the blue dye precipitate and will undergo a like reaction in the region below where the blue formed. In this manner the layer can be dyed in strata.

The solution of the first two phases of the general problem taught Dr. Gaspar how to convert a silver image into a colored one. The next problem is the practical application of the technique to color photography and color reproduction. To this end it is essential to prepare a three-layered monopack, whose separate entities will fulfill the requirements of subtractive-color synthesis. This means that each layer should be capable of registering a single color primary, and should yield a monochrome image which is the complement of the primary so registered. Offhand, these stipulations should not create much hardship. The blue-sensitive layer should be colored yellow, the green-sensitive portion should be colored magenta, and the red-sensitive stratum should be colored cyan. If the three layers are superimposed in the order yellow, magenta, cyan, each layer will register the complementary primary, and allow the other colors to pass practically unhindered to the next layer, minus the blue light which would otherwise severely interfere with proper

color selection. Where the film is to be used in the camera, this order and correspondence must be followed. The quality of the image formed is considerably below par, however, under such conditions.

Consider the effect of exposing a yellow-dyed emulsion, with blue light. An ordinary negative emulsion contains approximately equal weights of gelatin and silver salts. However, silver bromide has a specific gravity of 6.47 while gelatin has a specific gravity of about 1.00. This means that the relative volume occupied by the silver is one-seventh that of the gelatin, so that in any one direction, the ratio of the path of the light traveling through the dyed gelatin to that through the silver halide is more than two to one. When blue light is incident upon such a layer, a considerable length of gelatin must be traversed before the light reaches the light-sensitive elements. During this passage, the light is absorbed by the dye, so that when the silver-halide layer is reached, the intensity of the blue has been reduced considerably. The net effect is that no density can be developed that will correspond to a deep black, if we are dealing with positives, or a highlight if we are dealing with negatives. The contrast of the image becomes reduced to a degree that makes good images practically impossible. For the same reason, considerable emulsion speed is lost, for the light absorbed by the gelatin is of no value whatsoever for image formation.

The obvious solution in the case where negatives are to be made by this means, is to dye the film after the exposure has been made, so that no light would be lost during the exposure stage. How this can be accomplished was outlined in the discussion above. In the main, the procedure is to add colorless dyestuff-formers to the emulsion, and, after the exposure, treat them to form the dye. Often such after-treatment may interfere with the latent image. In that case the dyestuff-formers can be stabilized against developing and fixing baths, and dye formation made to take place after the silver image has been formed.

When the film is to be used as a copy material, an entirely different story is true. First of all, color correctness is not essential in the master from which the copies are to be made. It is important only that the differential absorptions and transmissions of the three part images be such that they print in different layers in the copy material. Since the coloring and sensitization can be controlled at will, it can be arranged that the top yellow-dyed layer be made red- or green-sensitive. These colors will not be absorbed by the yellow, hence will produce a latent image throughout the entire depth of the layer. Thus there is no great loss of speed or of contrast. In order for the exposing light not to affect the layer underneath, that layer must be dyed with a color which will absorb the red or green used to expose the top layer. By careful choice of dyes and sensitizers, it can be arranged that each layer in the pack will be exposed by a light that will be transmitted by that layer and absorbed by the layer beneath. The method for doing this is disclosed in United States patent 1985344, and its extension to printing from lenticular and screen plate originals

is disclosed in United States patents 1986054 and 1988891. The basic principles are discussed in the first mentioned patent (cf. also Eng. P. 408991, 409287, 415040, 441411).

The arrangements of the layers are such that consideration is paid not only to the absorption and transmission of each of the layers, but also to the relationship which must exist between all the layers. Thus in one embodiment of the invention, three silver halide layers are poured one on top of the other, the bottom layer being colored cyan, the middle magenta, and the uppermost yellow. This last is made green-sensitive by the addition of pinaflavol or erythrosin. The magenta layer is made red-sensitive, while the bottom cyan layer is sensitized to the infrared. Most blue and green dyes transmit beyond 680 $m\mu$ quite freely. Each of the colored layers acts also as a protective filter for itself and for the layers underneath. Thus the yellow dye in the top layer acts as a minus-blue filter for the entire emulsion pack. The magenta layer in the center prevents the green printing light used to form an image in the uppermost emulsion layer from registering in the central layer, which, if sensitized by means of pinacyanol will have a weak green sensitivity in the regions 500 to 520 $m\mu$ and 575 to 600 $m\mu$. In the same manner the cyan dye in the bottom layer will act as a barrier to whatever red light may spill over the exposure of the central layer. All three of the dyes freely transmit the infrared so that there will be no barrier to its passage. Only the bottom layer has infrared sensitivity, so only this layer will register an image.

A pack of this type is ideal when printing is done in stages from separation positives. It can also be used for printing from a colored master positive. This can be done if the blue-filter separation is converted into a color which will transmit red and infrared, but which will be modulated by green. A magenta or red is such a color. The green-filter image must be printed by red light, but must be transparent to green and infrared. A cyan color would serve here, if it is transparent to the infrared. But then most dyes are. The red-filter image must be printed with infrared light, and be transparent to red and green. The patent specifications mention naphthol green for this, and the claim is made that, in somewhat weaker concentration, this dye has high transmissions from 650 $m\mu$ downward. This is a rather broad statement, and somewhat questionable, since the green character of the dye is indicative of red absorption. The "Handbook of Chemistry and Physics," (Chemical Rubber Publishing Company, 13th edition, p. 951) gives this dye a maximum transmission of 36 per cent at 540 $m\mu$, dwindling down to one per cent at 640 $m\mu$, and only seven per cent at 600 $m\mu$. However, there are no doubt many substances which will absorb only in the infrared, and which would therefore serve.

When the material is to be used for printing from lenticular positives, the banded series of filters must not be the familiar red, green, and blue set. The blue must be replaced by a green filter which is opaque to the infrared, the green sector must be replaced by a red which is opaque to the infrared, and

the red by an infrared which is opaque to the visible (U.S.P. 1986054). In making duplicates from screen plates, where the screen is separated from the emulsion, as in the Finlay rather than the Dufaycolor techniques, a separate copying screen is used, with a pattern that is identical to that of the original, but having filter elements transmitting green, red, and infrared, rather than blue, green, and red (U.S.P. 1988891; Eng. P. 369616, 406294). No mention is made as to how such a screen could be prepared.

Another attack on the problem of correlating the spectral sensitivity of the layer with the color of the dye dispersed within that layer is made in United States patent 2075191 (Eng. P. 446206; Ger. P. 636185; Fr. P. 784518). Instead of shifting the sensitivity of each layer toward the red, the layers are dyed weakly, and instead of having the emulsions on one side of the base, they are coated on both sides, each side containing the three layers. There is insufficient yellow dye to prevent the blue light from reaching through the entire depth of the yellow layer, and a similar condition holds with the magenta and cyan layers and green and red light. But instead of printing one image, two identical images are printed on each side of the base. When the two weakly colored images are combined, the effect will be that of a strongly colored image.

It may be easier to utilize a duplitzed monopack, in which two layers are coated on one side of the base, and a third layer on the other side (U.S.P. 2183393). The two outer layers are colored magenta and cyan, while the central layer is colored yellow. This means that two of the layers could be printed by means of blue light, and since both the magenta and cyan transmit blue freely, no loss of contrast would be had. Of course, each printing must be done separately, but this is a preferred method anyway. The central yellow layer forms a barrier for the further passage of any blue rays that may spill through the magenta or cyan layers. The yellow layer could be sensitized to the infrared, or to the red. Many other arrangements of sensitizations could be had, which would allow the differential copying of the three partial images.

The preparation of a monopack suitable for two-color work, has also not been overlooked (U.S.P. 2028279; Eng. P. 412950; Fr. P. 746644). But instead of coloring each layer with a single dye, two are used. Thus the orange-red layer will contain pyramine orange and azo fuchsin, or azo fuchsin and mordant yellow, while the green layer will contain benzo pure blue and pyramine orange or benzo pure blue and metanil yellow. The rate at which the two dye components are acted on by the bleach solutions varies with the dyes. Thus it becomes possible to obtain dichroic effects in each layer, orangy highlights with deep red shadows in the orange-red layer, and sky-blue highlights with deep green shadows in the other. It becomes possible in this manner to obtain pleasant flesh and sky renditions, and at the same time, maintain true blacks in the middle tones and shadows. Such a process could be termed "two and one-half color."

A specific and detailed study of the entire problem of the relationship between the sensitivity of a given layer and the spectral absorption of the

color it must have in order to retain good contrast and balance, is contained in English patent 485552. Other types of monopacks are outlined in United States patent 2193931 and in English patents 445959 and 503330. The last is especially interesting in that it takes advantage of the difference in the spectral sensitivities of silver bromide and silver chloride emulsions. The first has a sensitivity going to 520 $m\mu$, while the last has a limit at 435 $m\mu$. If a silver chloride emulsion is made green-sensitive, it will have a sensitivity gap from 435 to approximately 520 $m\mu$. It becomes possible, then, to print through a yellow filter which absorbs the light up to 435 $m\mu$. The range from 435 to 520 will serve to print on to an unsensitized or color-blind silver bromide emulsion, while the range beyond 520 will act only upon the sensitized silver chloride.

A monopack that is suitable either for use in the camera, or for the making of a master positive for subsequent printing, is disclosed in United States patent 2166049 (Eng. P. 483366, 483463, 483464). The layers are coated in the following manner: A blue-sensitive emulsion is coated on to a celluloid base. The emulsion is not dyed, but contains dye intermediates which can easily be converted into a yellow dye at a later stage. Upon this is coated a layer containing a yellow filter dye, then a green-sensitive emulsion containing colorless intermediates for the formation of a magenta dye, and finally a red-sensitive emulsion. After the exposure, the pack is treated to form the dyes in the blue and green-sensitive layers. The top layer, which is undyed, contains a precipitant for a cyan dye, so that this layer can be dyed without affecting the other two. Thus a colorless pack receives the exposures so there is no loss of speed nor of contrast. The formation of the dyes and the preferential dyeing of the uppermost layer is accomplished by the methods outlined earlier in this chapter. It is to be noted that the blue-sensitive emulsion is on the bottom. This means that the pack is to be exposed through the carrier side. Since the processing yields a direct positive, there is obtained an inversion of right and left. This is rectified by exposing through the base, rather than in the normal manner.

Dr. Gaspar also suggested that the dye-bleach monopack could be used as one element of a Troland bipack. Here, it may be recalled, a bipack is formed with a two-layered monopack as one of the elements. Several different possibilities suggest themselves as to the arrangement of layers. In five of the six arrangements, two of the layers are separated by the thickness of one of the supports. In these, one of the elements is a single-coated film, the other contains coatings on both sides of the carrier. Obviously this leads to poor definition and a possible loss of registry for the layer that is so separated. The sixth arrangement is the conventional one where the two supports form the outside surfaces, and the three emulsion layers are one directly behind the other. The front element contains a single emulsion layer, and is colorless. The rear element is a two-layered monopack, dyed and processed in accordance with the Gasparcolor technique (U.S.P. 2183394; Eng. P. 446392, 450685).

A procedure as complicated as this usually involves some special technique

to make it work. Thus it has been found desirable to print the silver images very deep, much deeper than is required for the destruction of the dye. This enables the technician to cut down the time of treatment in the dye-bleach bath. The excess silver could then be removed by treatment with

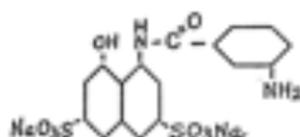
Copper sulphate	20 parts
Sodium chloride	20 parts
Nitric acid	1 part
Water to	100 parts
or	
Cupric chloride	30 parts
Nitric acid	1 part
Water to	100 parts

For some reason or other this was considered of sufficient importance to protect by patent (U.S.P. 2042253; Eng. P. 416666; Fr. P. 751932). Another source of trouble lay in the creeping of the dyes in the bottom layer into the support or the backing. To offset this it was proposed (U.S.P. 2088523; Eng. P. 444669; Fr. P. 785525) to add a layer of colloidal silver or exposed silver halide between the bottom layer and the support. What dye creeps in will now be destroyed in the dye-bleach.

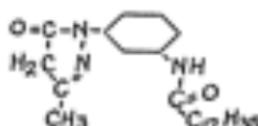
The improved character of the image when a black-and-white key plate is present, has also been noted. To take advantage of this, a silver halide layer dyed black, and sensitized to a region of the spectrum different from the other three layers, is incorporated into the film. This can also be used for the formation of a black-and-white sound track (U.S.P. 2125015). The corresponding sound track area in the other three layers could be given overall unmodulated exposures to produce a uniform destruction of the yellow, magenta, and cyan dyes, thus leaving only a black dye image. In another disclosure (U.S.P. 2132154) it is proposed that the pack be exposed and developed, but not fixed. It is then treated with the dye bleach to form the color images. The remaining unexposed silver salts could then be converted into a positive black-and-white key plate. If a silver sound track is desired, the three colored emulsions could be given a uniform exposure in the sound track area, developed and processed to destroy all the dye in this region, then rehalogenized to reform silver bromide. This can now be exposed to the sound negative and processed to a black-and-white silver image. Sound track problems are involved in the following disclosures

<i>United States</i>	<i>English</i>	<i>French</i>
2025658	412949	745934
2062304	413688	746426
2136143	432464	
2155894	468508	
	468509	
	472644	
	472981	

After Dr. Gaspar demonstrated that silver-dye-bleach processes were entirely feasible, other experimenters began to play with it. Chief among these were Agfa, and, more lately, the Eastman Kodak Company. Agfa had already solved the general problem of dispersing a substance evenly throughout a layer (cf. chapter on Ansco Color). It may be recalled that their method consisted in adding extremely heavy groups to the molecule to make it substantive, or at least non-diffusing. A complete specification for a monopack is disclosed in English patent 488853. The red-sensitive layer contains the 3-amino-benzoyl derivative of H acid



The green-sensitive layer contains a stearyl-amino phenyl derivative of pyrazolone,



The blue-sensitive layer contains, besides a yellow filter dye, di-(aceto-acetyl)-benzidine



These substances are colorless, hence have no effect upon the exposure. After exposure and development, the film is treated with tetrazotized benzidine. The substituted H acid couples to form a cyan dye, the pyrazolone compound will form a magenta, and the benzidine couples to yield a yellow, all the colors diffusely coloring each layer. These dyes are next treated with a bleach solution, compounded by mixing equal parts of A and B (U.S.P. 2100594; Eng. P. 375338, 401340)

Solution A

Potassium iodide	33 parts
Iodine	17 parts
Sulphuric acid, concentrated	525 parts
Water to	6250 parts

Solution B

Sodium sulphite	33 parts
Thiourea	33 parts
Water to	6250 parts

Dyes suitable for this procedure, beside the ones formed above, are

Congo pure blue
Sirius ruby violet R
Sirius ruby B
Sirius yellow
Chrysophenine G

and any other azo dyes which can be readily reduced by sodium hydrosulphite to yield colorless products.

A more normal type of monopack is disclosed in English patent 454088. This is a duplitzed type of monopack, containing a blue-sensitive layer on one side of the carrier, which has been dyed cyan with Chicago blue. On the other side is coated a red-sensitive emulsion dyed magenta with Sirius ruby. On top of this is coated an uncolored blue-sensitive layer. Thus it is possible to print two separations on the two outer layers by means of blue light, and the central layer by means of red light. After exposure and development, the top uncolored layer is dyed yellow with chrysophenine yellow, after which the dye is bleached in situ with the silver image in accordance with the methods outlined above. The danger of dyes diffusing from one layer to another is minimized by dyeing each layer with a mixture of acid and basic dyes in such proportion that mutual precipitation takes place (U.S.P. 1954294; Eng. P. 372620).

In another disclosure, a monopack built along duplitzed film pattern is described (U.S.P. 2020607; Eng. P. 379934). The cyan layer is colored with brilliant benzo fast green, the magenta with Sirius red violet R, and the yellow with benzo light yellow RL, or chrysophenine G extra. After exposure and development, the pack is not fixed, but is treated with the dye-bleach bath. The unused silver is then removed, and the unfixed silver halide exposed and developed to yield a black-and-white key plate (U.S.P. 2169320; Eng. P. 506359). It is quite surprising how close these procedures are to those disclosed by Dr. Gaspar. The method for forming a sound track is disclosed in English patent 483052.

The Eastman Kodak Company, especially the English subsidiary, has been issued a series of patents that deal generally with monopacks, whose processing is a combination of several techniques, including silver-dye-bleach (Eng. P. 468560, 475784, 475786, 477524). A patent issued to Dr. M. W. Seymour of the same company would utilize the vat dyes for coloring the layers (U.S.P. 2184022). Gaspar had first proposed to do this. But Dr. Seymour extends the list considerably. Indanthrene yellow (Schultz No. 1220), algol pink BBK (No. 1221), algol red BTK (No. 1261), indanthrene blue 5G (No. 1238), and caledon blue 3G (No. 1232) are some specific examples. For a three-color system, it is possible to use indigo for the cyan, algol pink BBK for the magenta, and indanthrene golden yellow or algosol golden yellow for the yellow.

After exposure, development, and fixation the dye can be bleached by treatment with one or the other of the following solutions:

1. Potassium sulphide	2½ parts
Sodium hydroxide	2½ parts
Water to	100 parts
2. Potassium cyanide	5 parts
Pyridine	5 parts
Water	100 parts
or	
3. Stannous chloride	8 parts
Sodium hydroxide	10 parts
Triethanolamine	10 parts
Anthraquinone	0.0025 part
Water to	100 parts

The anthraquinone is present probably as anthrahydroquinone. Its presence helps to keep the highlights clear.