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### Organic Sulfur Compounds in Silver Halide Photography

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# ORGANIC SULFUR COMPOUNDS IN SILVER HALIDE PHOTOGRAPHY

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*(Received 26 January 2001)*

The diversity of functions of organic sulfur compounds in the most important fields of silver halide photography is reviewed. While organic sulfur compounds of the lower oxidation states (–2 to 0) are discussed mainly as important ligands for silver ions in all stages of the photographic process, those of the higher oxidation states (+2 to +4) are shown to be useful for modifying the reactivity and physical properties of auxiliary and supplementary components.

**Keywords:** Photography; Thiols; Thiones; Thioethers; Disulfides; Sulfones; Sulfonamides; Couplers

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## 1. INTRODUCTION

Silver as a rare element and noble metal has been long studied in its natural deposits. There has been much concern about the dwindling hoard of silver [1]. Since about 1970 the photographic industry, which had been one of the main consumers of silver, has developed the capability for recovering 99 per cent of all silver entered into the production of photographic materials, and might have a clear conscience. There is no more wondering about its whereabouts. In 2000, the perspectives of growing silver demand have faded, due to the steadily growing share of electronic photography.

To mention the economically most important source of silver, the precious metal occurs as a contaminant in sulfide ores, e.g. in "argentiferous" galena, depending on the origin of the ore deposit. True silver ores such as those of ancient Saxony, Hungaria or Peru are no more available.

Galena of sedimentary origin is found less argentiferous than galena of hydrothermal or even magmatic origin. What is need in nature to mobilize silver within the catchment area of deep-ocean hydrothermal vents is a suitable concentration of thiosulfate and/or chloride, as it is found in "black smokers" where the formation of ore minerals is induced by rapid cooling in seawater and can be recognized on site [2]. Thus, silver has been found close to the earth's surface from the beginning, and most of the available silver appears to have been mined in the past. No doubt, silver will remain a precious metal also in near future.

As a silver ligand, the sulfur atom is much more versatile than a halogen atom, at least in organic sulfur compounds, and it depends mainly on additional ligands bound to sulfur what bond formation between the silver ion and sulfur can effect. The reader is invited to enter one of the most interesting domains of organic sulfur chemistry: silver halide photography, and to look at it under the aspect of its diversity.

Within the context of this review, it was preferred to discuss the role of organic sulfur in photography according to the variety of tasks emerging in all stages of the

production of a photographic image. The general principle was that of identifying:

- photographic challenges and chemical problems on the one hand, and
- surprising solutions based on sulfur compounds on the other hand,

with the focus mainly on color photography where the sequence of steps is the longest and most complex, where the highest degree of integration and sophistication in photographic systems is found and the economic constraints are hardest and least avoidable, while disregarding systems such as thermographic print-out materials.

Starting from general topics of sulfur reactivity, such as redox chemistry, as an alternative principle, and allocating photographic problems to items of sulfur chemistry, might have increased the risk of redundancy, while the reader would have been left without a chance of getting familiar with the fascinating aspects of image formation in photography.

However, an overview presenting the complex system of silver halide photography together with processing will not be given, and apart from selected topics such as dye formation, neither aspects of solid state physics nor practical aspects of photographic design will be discussed in any depth. Consequently, the interested reader will be referred to surveying the literature [3].

## 2. ORGANIC SULFUR COMPOUNDS IN EMULSION MANUFACTURING

The manufacture of light-sensitive silver halide emulsions comprises at least three subsequent steps where sulfur compounds are involved and possibly play a key role, by essentially controlling the quality profile of the finished “emulsion”, a dispersion of sensitized silver halide microcrystals. These steps are:

- precipitation (nucleation) and growth,
- removal of soluble by-products (essentially neutral salts),
- chemical sensitization,
- spectral sensitization.

### 2.1. Organic Sulfur Compounds in Silver Halide Precipitation

#### 2.1.1. Organic Sulfur Compounds as Growth Modifiers for Silver Halide

In the manufacture of light-sensitive silver halide emulsions, the dispersity of grain size and also of sensitization has been identified as a major drain of photographic speed. Silver halide microcrystals of high-speed emulsions for color film show a layered structure in their interior, to provide ready separation of the charge carriers formed by exposure and efficient latent image formation. One of the best known processes for preparing coarse-grained silver bromide (iodide) emulsions consists in dissolving an added ultra-fine-grain emulsion of the Lippmann-type in the presence of “seed crystals” designed to grow to the desired grain size and aspect ratio (“state-of-the-art” coarse-grain tabular emulsions show an average size of 1–2.5  $\mu\text{m}$  and an aspect ratio between 5:1 and 12:1).

Hydrophilic *bis*-thioethers such as **1** and **2** (Fig. 1), where the thioether groups are separated by two aliphatic carbon atoms, provide a ligand structure for silver ions

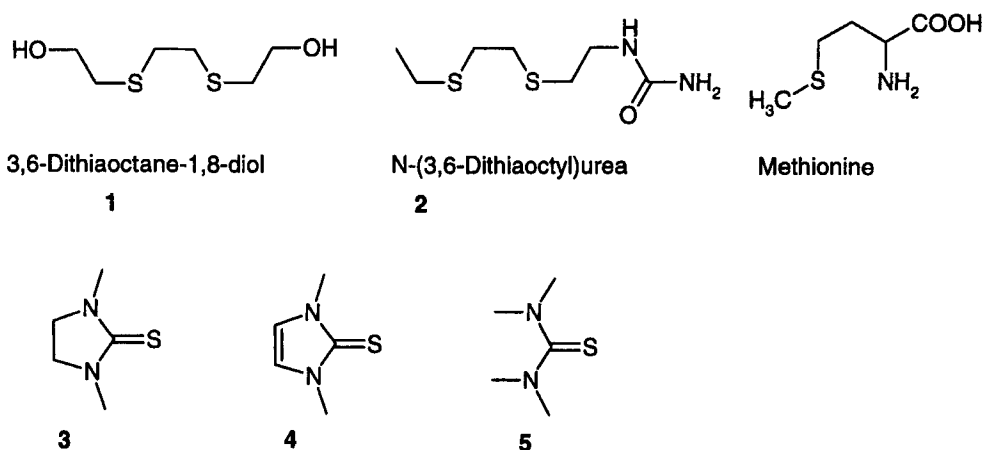
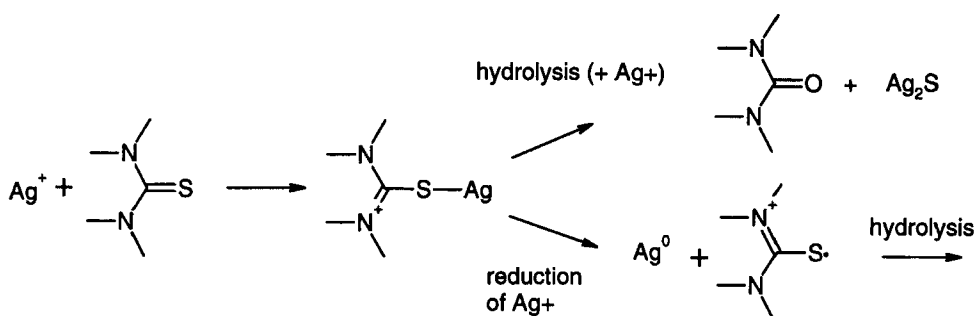


FIGURE 1 Growth modifiers/complexing agents for silver halide emulsions.

FIGURE 2 Slow reactions of tetrasubstituted thiourea with Ag<sup>+</sup>.

which favors the growth of bigger crystals at the cost of decisively smaller microcrystals and even helps to dissolve any small microcrystals [4]. As a consequence of enhanced recrystallization, the dispersity of the grain population of a single emulsion is diminished.

Substituted, and preferably cyclic derivatives of thiourea, such as **3**, **4** and **5** (Fig. 1), have been claimed likewise as useful additives for recrystallization, and they strongly influence the electronic properties of the microcrystals [5]. It is known that their presence on the grain surface may lead to diminished raw-stock stability and increased thermal fogging, i.e. development without exposure. Increasing the degree of substitution of thiourea leads not only to an increase in stability to hydrolysis, but also to an increase in reducing capability. Thus, the desired advantage of higher stability to hydrolysis may be compensated by an increased tendency to undergo hydrolysis as the consequence of slow electron transfer. Bond formation between silver ions available from the surface of a silver halide microcrystal and a thione group bound to nitrogen contributes to slow hydrolysis of the thione, with formation of silver sulfide [6]. Under *in vitro* – testing conditions (70–80°C) the reactions between soluble Ag<sup>+</sup>-salts and ligand (Fig. 2) can be observed in gelatin solution.

### 2.1.2. Hydrophilic Copolymers as Peptizing Agents for AgX-Containing Thioether Moieties

Research Disclosure 22534 (1983) cites more than 70 US- and UK-patents claiming the use of synthetic colloids, to replace gelatin as the protective colloid in the emulsion precipitation step. The colloid must be stable and has to prevent the silver halide microcrystals from undergoing coalescence, leading to formation of larger aggregates.

In manufacturing silver halide emulsions and coating solutions, gelatin has to:

- regulate crystal growth,
- prevent agglomeration of grains,
- prevent formation of new crystallization nuclei,
- support the desalination procedure, e.g. by reversible flocculation,
- regulate the rate of chemical and spectral sensitization,
- prevent formation of spontaneously developing silver clusters on the crystal surface,
- prevent regression of latent image,
- form a jelly at temperatures below 36–38°C within an acceptable period of time.

As a natural product, photographic gelatin is made from animal skin or bones, and its quality depends on standardized production processes. In addition, it is unstable to acid and alkaline media and provides an excellent nutrient for microorganisms.

Obviously, there were good arguments in favor of replacing gelatin by tailor-made polymer peptizing agents. The demand for synthetic polymers emerged at an early stage and different concepts were investigated. Apparently, none of these innovative products has reached the stage of industrial production. Since only partial aspects of this item have been investigated in the laboratories of Agfa-Gevaert, it may be reported by way of a close-up and from arbitrarily selected evidence, at a distance of about twenty years.

Acceptable hydrophilic colloids have been available as synthetic silver halide peptizing agents, and many of them were synthesized by making use of a hydrophilic copolymer backbone **9** derived from acrylamide, acrylic or methacrylic acid, additional “modifying” monomers such as acrylates, sulfonated acrylic monomers, *N*-vinylpyrrolidone, 4-vinylpyridine and vinyl ethers. Extensive use has been made of polythioether groups from vinyl sulfides [7], to establish the desired “amphiphilic character” of the peptizing agent (Fig. 3).

As the most efficient principle for incorporating “argentophilic groups” into a hydrophilic copolymer a method was devised, whereby mixtures of the respective monomers and polythioether-polythiols such as **6**, **7** and **8** were copolymerized in a suitable solvent such as *tert*-butanol and in the presence of radical initiators such as azo-isobutyronitrile or *tert*-butyl-peroxyoctanoate [8].

The polymers were obtained as non-hygroscopic white powders in high yield, usually 85% of the theoretical or higher. The designed “argentophilic units” (a hypothetical composition is represented in Fig. 3) were incorporated quantitatively by chain transfer, as shown by the sulfur content, approaching theoretical values. It is assumed that thiol groups are capable of entering polymerization as radicals where a polymer chain is attached. Measurements of intrinsic viscosity showed that the molecular weight of the polymers was low, usually below 15,000, and their function was interpreted more as that of a polymeric surfactant. The polymers were readily dissolved in water and found miscible with gelatin even in the dried state.

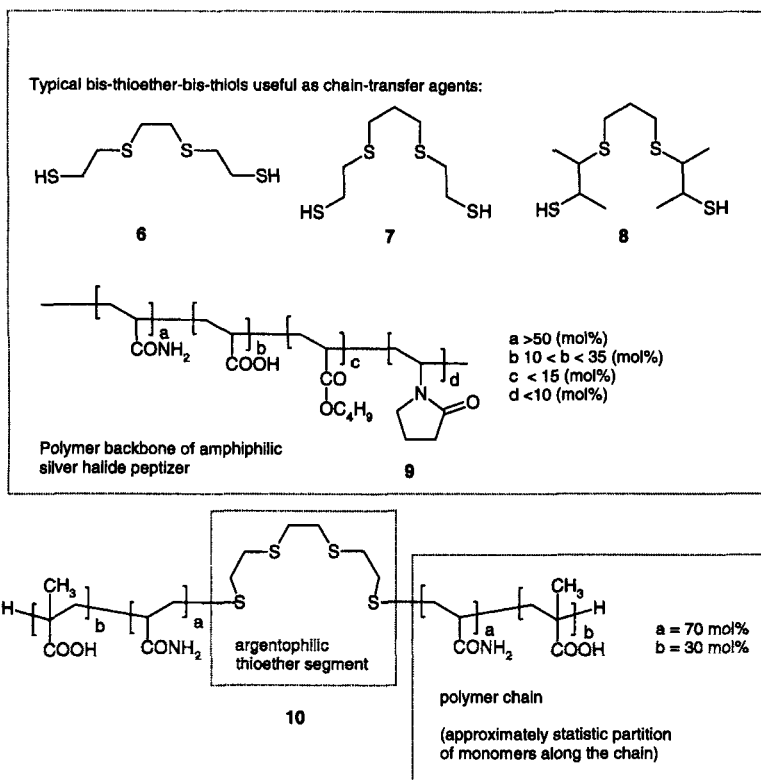


FIGURE 3 Polymer peptizing agents.

A copolymer **10** (Fig. 3) consisting of 70 mol% of acrylamide and 30 mol% of methacrylic acid, prepared by polymerization in the presence of 0.02 mol of 3,6-dithiaoctane-1,8-dithiol per mol of monomers, was found suitable for preparing a heterodisperse silver bromide-iodide emulsion containing 6 mol% of iodide, in the presence of 3.2 or 6.4% by weight of the polymer (preparation by two-step addition of silver nitrate solution to an aqueous polymer solution of sodium bromide and potassium iodide at 50–85°C at pH 6 to 6.5 and subsequent flocculation by addition of acid, at pH 3). Favorable amounts of polymer were 3–10% by weight, higher contents of polymer led to restrained crystal growth. An example of a polymer-peptized silver bromide-iodide emulsion prepared at 70°C in the presence of 3.2% by weight of polythioether-copolymer **10** (70% acrylamide, 30% methacrylic acid and 2% *bis*-thioether-*bis*-thiol I) is shown in Fig. 4 (original scale 1 : 10,000).

When the experiment was repeated under darkroom conditions [9] at 50°C and the resulting emulsion was flocculated in the presence of gelatin and sulfonated polystyrene, its photographic speed in unsensitized state was found approximately equal to that of a gelatin-peptized emulsion which had undergone chemical sensitization by thiosulfate plus gold(I). The average grain-size of the polymer-peptized emulsion was found lower than that of the gelatin-peptized emulsion, its microcrystals appeared rounded, and in black-and-white development the slope of the characteristic curve was found steeper. Subsequent chemical sensitization by Au(I)/thiosulfate led to fog and loss of photographic speed. As the most unexpected feature an inherent



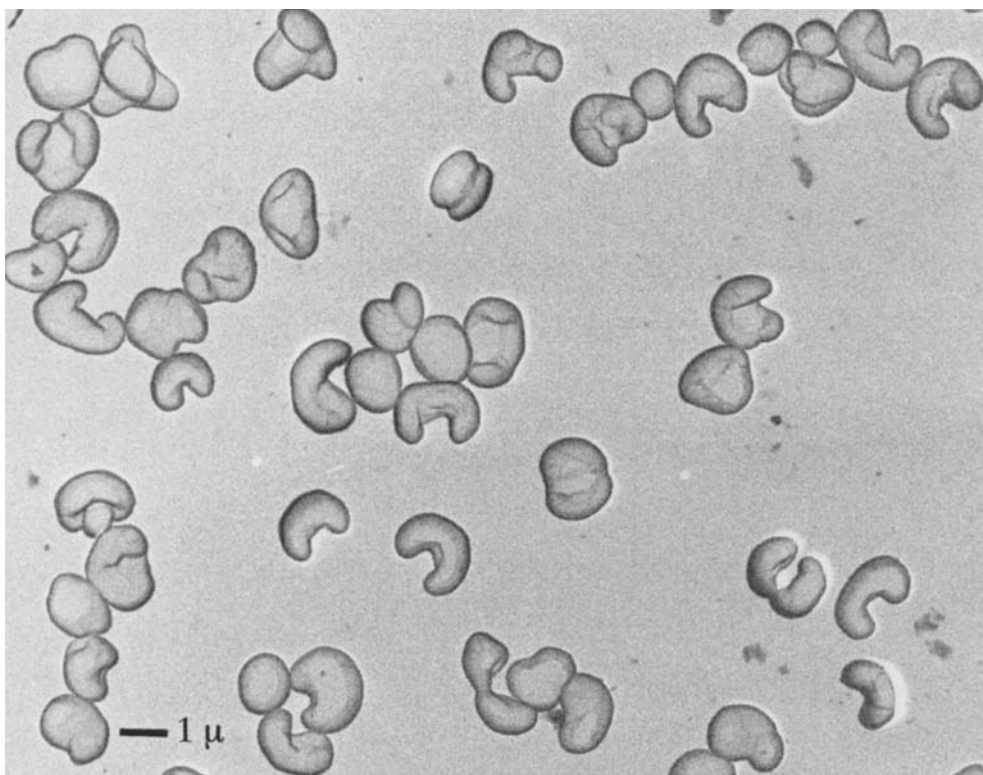
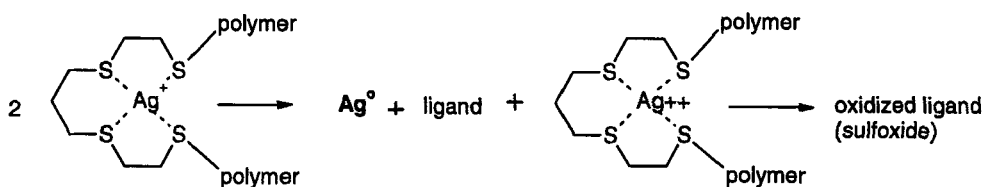


FIGURE 4 Polymer peptized AgBr(I) emulsion.

FIGURE 5 Formation of  $\text{Ag}^0$  by ligand-induced disproportionation.

red-sensitivity of the polymer-peptized emulsions was detected, an unmistakable instance of reduction-sensitization which was tentatively explained by ligand-induced disproportionation, as exemplified in Fig. 5 [10].

To obtain polymers similar to non-sensitizing gelatin, a different approach had to be taken, by copolymerization of added allylammonium chloride, to make use of the peptizing capabilities of primary or secondary amino groups. Salts of allylamine and diallylamine are well known for their sluggish copolymerization [11]. This does not apply when the copolymerization is carried out in the presence of small amounts of thiols or *bis*-thiols (about 10 mmol per mol of monomers). Smooth copolymerization was achieved in approximately the same way when cyclic disulfides such as thioctic acid were used as polymerization-mediating agents. Among the *bis*-thiol-type chain transfer reagents used, several heterocyclic *bis*-thiols have also been investigated in

combination with monomer mixtures based on acrylamide, acrylic acid and optionally a neutral monomer such as *N*-vinylcaprolactam, and some compounds have been found to show acceptable performance as synthetic peptizers for light-sensitive silver halide emulsions.

To avoid undesired sensitization induced by the polymer, the principle of thiol-mediated copolymerization was abandoned: thiols as chain transfer reagents were replaced by compounds containing a P–H bond, such as dialkyl phosphonate [12]. Again, the copolymers were isolated in high yields as white powders, containing up to 50 mol% of allylammonium salts, provided the content of acrylamide was higher than 40%. However, at an allylamine content higher than 30 mol%, the polymer yields dropped to about 60% of the theoretical.

The silver halide peptizing capabilities of copolymers containing 15–25 mol% of allylammonium salt, 15–25 mol% of acrylic or methacrylic acid and 50–70 mol% of acrylamide was found comparable to that of inert gelatin, and there was no observable premature sensitization.

## 2.2. Organic Sulfur Compounds in Chemical (Emulsion Ripening) and Spectral Sensitization

It is well known that non-sensitized silver halide microcrystals do not exhibit a low threshold of exposure to make the crystal developable [13]. Of course, pre-exposure would be the best means to make exposure more efficient, and this might have been the only reason for the success of the first known experiment on color photography: J.C. Maxwell's historical demonstration of the color separation principle [14] was performed at a time when neither spectral sensitizing of silver halide nor chemical ripening or gelatin as the binder were known, and it was carried out by use of inadequate equipment. Maxwell's experiment might have succeeded for different reasons, none of them trivial.

Contemporary high-speed consumer materials such as 800-ASA color negative film contain silver halide microcrystals capable of undergoing development as the consequence of three to four subsequent "hits" by light quanta, and there is confidence within the scientific community that this threshold can be lowered to a clean "two-quanta-process".

Of all theories in discussion, the Mitchell-concept of latent image formation [15] provides the most comprehensible and consistent rules for understanding the primary processes of charge separation (e.g. mobility of "photoelectron" and "hole") and provides instructions for appropriate design of silver halide grains, including chemical and spectral sensitization of photographic emulsions. Mitchell emphasizes the role of the stable silver dimer  $\text{Ag}_2$  in latent image formation, and that of silver sulfide produced by "chemical ripeners" as hole traps.

### 2.2.1. Thione Type Chemical Sensitizers: The Problem of Replacing Thiosulfate as the Ripener

To understand the unique role of sodium thiosulfate as a "ripeners" it has to be considered that sodium thiosulfate is adsorbed before it reacts with interstitial silver ions at the grain surface. The latter reaction appears to be slow. An increase in speed is obtained by additional sensitization with complexes of Au(I), accompanied by better resistance

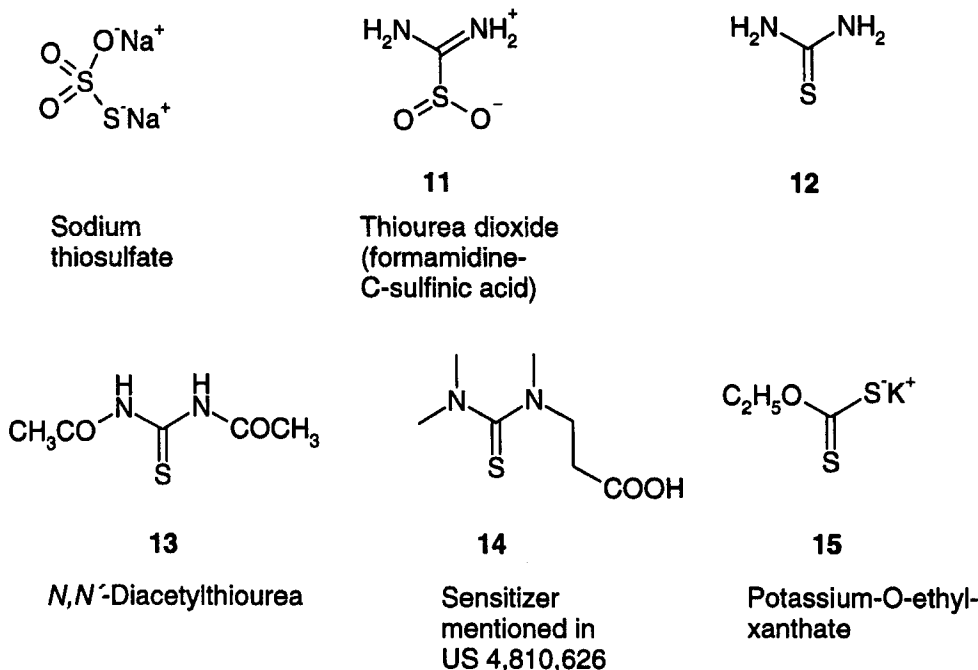


FIGURE 6 Chemical Sensitizers/Ripeners.

to regression of speed [16,17]. The concentration of sensitizing clusters at the surface of the silver halide microcrystals is usually in the range of parts per million or lower.

The reaction of free sulfide ions with silver halide proceeds considerably faster and leads to high fog level. It must be kept in mind that the sulfide ion is a powerful reducing agent. Considerable work has been carried out to find sulfide equivalents superior to thiosulfate. Pure reduction sensitization, on the other hand, is achieved by thiourea-*S,S*-dioxide (or formamidine-*C*-sulfinic acid) **11** (Fig. 6).

As exemplified by Fig. 6, derivatives of thiocarboxylic acids or thiocarbonic acid have been investigated as chemical ripeners, among them esters of dithiocarboxylic acids [18], thioamides, dithiocarbamates, dithiocarbonates **15** [19] and, with highest effort, derivatives of thiourea **13, 14**.

The use of thiourea and selenourea derivatives as chemical sensitizers has been claimed for several decades. It has never been clarified to what extent any of the compounds acts as a true chalcogen sensitizer and to what extent its sensitizing efficiency can be explained in terms of reduction sensitization. Moreover, certain tri- and tetrasubstituted thioureas, whose thione group appears very stable to hydrolysis, have been identified as supersensitizers [20], *N,N'*-Diacetylthiourea has been recognized as one of the "fastest" ripening agents known.

### 2.2.2. Dithiophosphates as Stabilizing Additives

In *O*-esters of dithiophosphoric acid, the stability of the phosphorus-sulfur bond appears to be high enough to prevent formation of silver sulfide, and they have been shown to keep the fog level during chemical sensitization low [21].

### 2.3. Organic Sulfur Compounds as Emulsion Stabilizers

The task of stabilizing a photographic silver halide emulsion presents different aspects:

- keeping photographic speed unchanged at high level,
- keeping fog level within admitted boundaries,
- keeping the slope of the characteristic curve unchanged,
- keeping the response of the emulsion to deviations in processing constant,
- keeping the pressure-induced fog or desensitization low.

#### 2.3.1. Stabilizers of the "Weak Oxidant" Type

In practice, most fog problems result from the struggle for more speed; overreduction can be avoided by derivatives of sulfenic acids, disulfides or thiolsulfonates. Suitable reagents of the "weak oxidant" type are listed below:

- 2,2'-Diindolyldisulfides [22],
- Disulfides plus Sulfinates, Cyclic disulfides, e.g. derivatives of thioctic acid [23],
- Dithione-1,1-dioxides [24],
- Isothiazolones [25],
- Diaryldisulfide, carrying carboxyl groups [26],
- Dehydrodithizone [27].

#### 2.3.2. Stabilizers of the Heterocyclic Thiol type, Preventing Fog and Loss of Photographic Speed

Apart from tetraazaindenes, most common emulsion stabilizers are of the heterocyclic thiol type (16–27, Fig. 7). The literature deals with single aspects of stabilization, but reviews are scarcely available [28]. Tani has demonstrated that most of the usual stabilizers of the thiol/thione type are absorbed with formation of an S–Ag-bond [29].

#### 2.3.3. Latent Image Stabilizers

The stabilization of the latent image is one out of many poorly defined goals in optimization of emulsions. It is commonly understood as one of establishing an adequately redox-buffered system.

Occasionally, reduction of aerial oxygen to hydrogen peroxide by scavengers of the hydroquinone type has been made responsible for latent image regression. Care has to be taken wherever a reducing agent is supposed to activate an otherwise harmless oxidant such as oxygen: heterocyclic thiols/thiones, and also disulfides can prevent the worst case from happening.

### 2.4. Organic Sulfur Compounds in Spectral Sensitization

#### 2.4.1. Spectrally Sensitizing Dyes (Fig. 8)

*2.4.1.1. Sulfur-containing Merocyanines and heterocyclic thiones as spectral sensitizers and supersensitizers* Merocyanines such as 28–32 are mainly used as sensitizers for black and white film and printing paper, for graphic and technical material. The number of technically important dyes is large. Typical sensitizing dyes of the

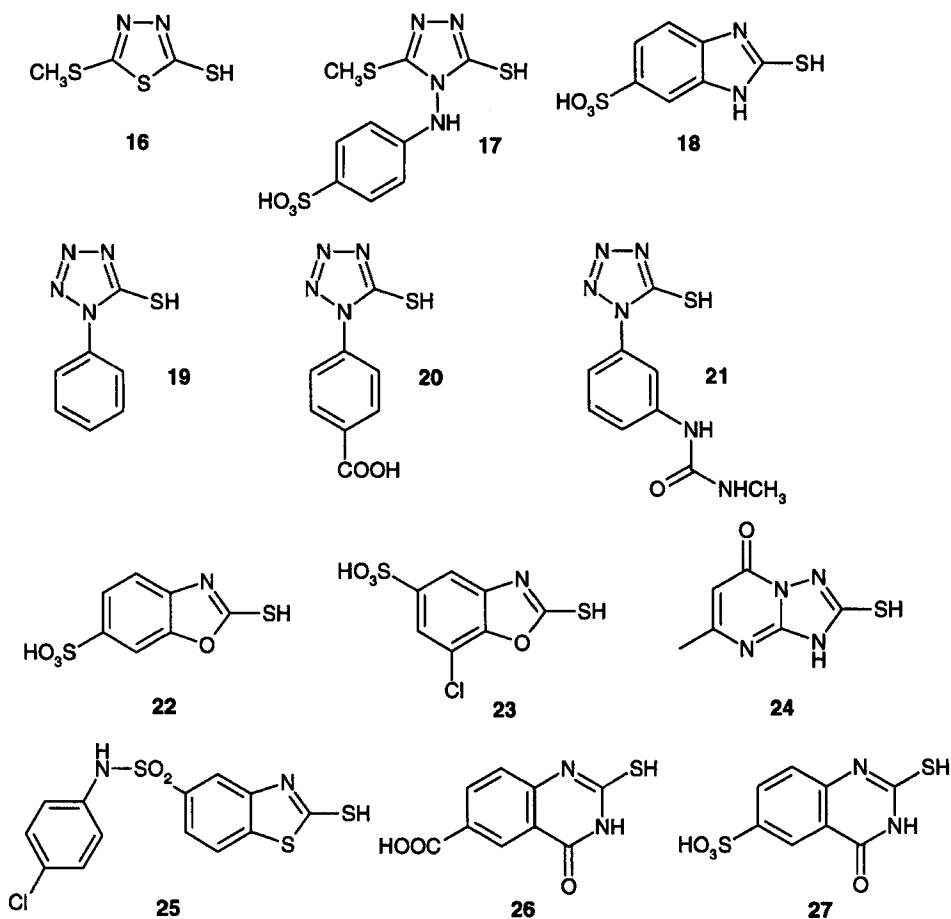


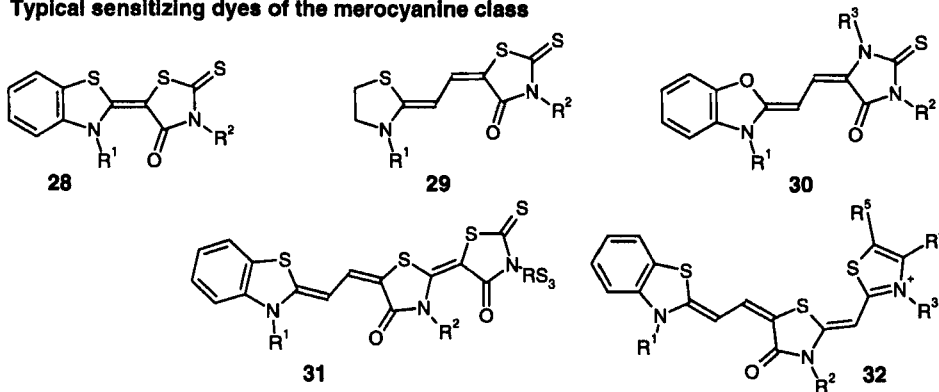
FIGURE 7 Tautomerizable thiol-type stabilizers.

merocyanine class are mentioned below. Many of them contain a thioether group as a part of a heterocycle and an additional sulfur atom as a part of a thione group.

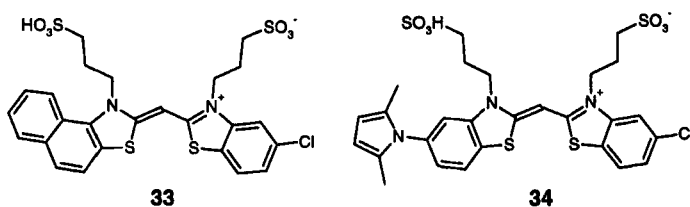
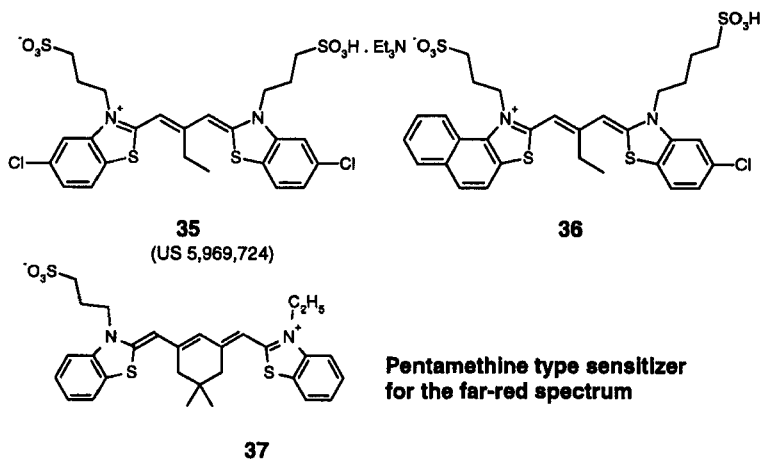
Heterocyclic thiones of the enolizable type (see **25**, Fig. 7) and of the non-enolizable type as well have occasionally been observed to act as supersensitizers. The supersensitizing effect may be attributed to the thione group in general.

**2.4.1.2. Sulfur-containing Cyanines/Benzothiazolium-(Thiacarbo)cyanines** None of the other classes of cyanine dyes enjoys such common use as cyanine dyes containing one or two benzothiazole nuclei (**33–37**): They are capable of sensitizing silver halide over the whole visible spectrum, from blue to infrared light, and with the unique efficiency of forming closely packed J-aggregates. These show narrow and steep sensitization bands with peak-shaped maxima enabling the emulsion chemist to place photographic sensitivity exactly where it is needed.

To make sure that aggregated sensitizing dyes are actually removed from processed materials, the dyes are preferably substituted by alkyl groups at nitrogen-containing anionic groups such as sulfonates.

**Typical sensitizing dyes of the merocyanine class**

$R^1 - R^5$  = Alkyl, optionally substituted by an anionic group  
 $X = O, S, NR^4$

**Typical blue sensitizers (monomethine type)****Typical red sensitizers (trimethine type)**

**Pentamethine type sensitizer  
for the far-red spectrum**

FIGURE 8 Spectrally sensitizing dyes.

In general, aggregation of sensitizing dyes leads to advantages in photographic performance: the injection of photoelectrons from excited J-aggregates of methine dyes proceeds with formation of electron-deficient "dye holes". On account of this, the overall reaction appears reversible under unfavorable circumstances. Loss of sensitizing efficiency is usually observed beyond an optimum value of dye coverage on the silver halide grain, mostly above 20%. Desensitization has therefore been attributed

at least partly to inadequate size of the aggregates whereby the catchment area for photoelectrons increases while the probability for electron injection by the aggregate remains unchanged.

The use of certain sensitizers of the pentamethine type, appears to depend on the presence of suitable heterocyclic thiones such as **25** (Fig. 7) which strongly enhance the sensitizing efficiency and have been named "potentiating compounds" [30]. Rather surprisingly, none of the known physical methods used for investigating dye aggregates adherent to silver halide discloses any recognizable differences in the adsorption state of the mere dye, compared to its "potentiated" equivalent.

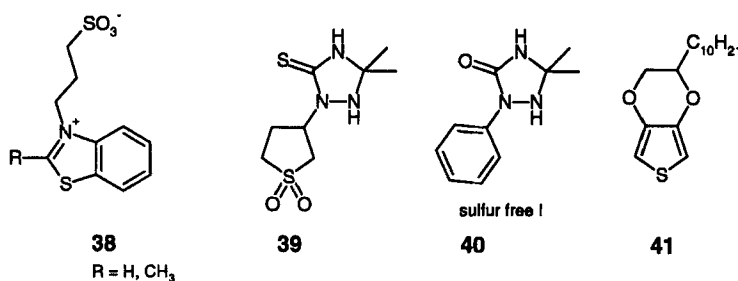
#### 2.4.2. Sulfur-Containing Supersensitizers (38–41, Fig. 9)

The concept of supersensitization by dye-hole trapping was formulated by Gilman [31]. It has been one of the primary efforts of supersensitization to increase speed, another one to extend the range of dye coverage by diminishing "concentration desensitization". Supersensitizing by thiourea derivatives especially of the heterocyclic thiourea type has been discussed above, in close context with ripening capabilities. In fact, it may be questioned if it makes sense to regard chemical sensitization and supersensitization as distinctively separate phenomena.

It has been shown that many supersensitizers increase the efficiency of sulfur sensitization, most possibly by reducing the mobility of holes – in much the same way as they reduce the life time of dye holes.

Phenothiazines [32] (Fig. 9) show high nucleophilic character and, when unsubstituted in ring position ortho and para to the nitrogen atom, are capable of coupling to dark-green azomethine dyes. Their cyclovoltammetric behaviour at pH 6.5 demonstrates that electron-transferring capabilities successfully compete with electrophilic

#### Supersensitizers



#### Supersensitization by phenothiazine

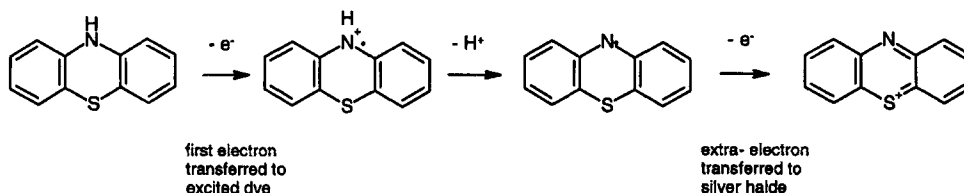


FIGURE 9 Sulfur-containing supersensitizers.

substitution: two electrons are reversibly transferred, but the electron transfer steps cannot be observed separately. US 4,607,006 discloses the use of *N*-substituted phenothiazine derivatives as supersensitizers, especially derivatives that bear an *N*-alkyl spaced thiourea group [33]. In a more recent disclosure [38], phenothiazines are disclosed among many other compounds bearing fragmentable groups.

It should be kept in mind that this three-step process involves four reactive species and leads to one half of a stable Ag<sub>4</sub>-latent-image center:

- the excited dye aggregate, which by accepting the first electron undergoes transformation to an anionic radical species,
- the supersensitizer, releasing an electron to the excited dye and forming a radical cation,
- the radical cation releasing a proton and an extra electron, and
- the silver halide, which as the result of two successive electron transfer steps is enabled to form one half of a stable Ag<sub>4</sub>-latent-image center.

Thiazolium salts and benzothiazolium salts **38** can be shown to sensitize an emulsion, in addition to sulfur or sulfur-plus-gold sensitization. The effect is most pronounced in spectrally sensitized emulsions. It has been claimed also that benzothiazolium salts are used as growth modifiers, capable of directing epitaxial growth of cubic satellite crystals on edges of larger silver halide crystals [34].

Supersensitization has also been shown to occur by addition of 1,3,3-trisubstituted triazolidinethiones **39** and triazolidinones **40** to a sensitized emulsion, where an increase in speed of 60% or even more has been found, in the triazolidinone series normally without concomitant increase in fog [35]. It is concluded that this type of supersensitization results from “extra-electron-transfer”.

Supersensitization by 3,4-alkylenedioxythiophenes **41** shows a somewhat different profile [36] in that the observed speed increase is normally smaller than that of triazolidinone-supersensitization, and more sensitive to increased fogging. For chemical reasons, it has to be supposed that only one electron is transferred to the excited dye aggregate, leaving a thiophenium radical-cation [37], corresponding to a theoretical 50% speed increase. Extra-electron transfer and an increase in speed of about one stop have been claimed by use of fragmentable electron donors, also within the phenothiazine series [38].

### 3. ORGANIC SULFUR COMPOUNDS IN PROCESSING

#### 3.1. Organic Sulfur Compounds in Development

To understand photographic development and the possibilities of influencing it, the fate of an exposed grain should be considered. In development, latent image nuclei formed by exposure are induced to take up electrons from the developer solution and undergo transformation into an electrode [39]. This step is vulnerable and most accessible to inhibition. At the end of the induction period, the “latent image” becomes “apparent” and a silver filament can be observed growing into the developer solution.

In an ordinary “chemical” developer, the growth rate of the silver filament is limited by the supply of silver ions from the interior of the grain, and those “latent image” silver nuclei may be preferably involved in development which are positioned next to



places of high mobility of silver ions, i.e. next to twin planes. Once this process has started, there should be few instances of taking influence.

In contrast to the chemical developer, most of the silver formed in a physical developer is transported to the point of deposition via the solution where sulfur compounds take part as silver complexing agents.

Among the most common development activating, fixation activating or even bleach activating additives for photographic processing solutions, alkali or ammonium salts of thiocyanic acid have to be mentioned although they are commonly classified as inorganic compounds. As derivatives of thiocarbonic acid, they are powerful silver complexants capable of dissolving silver halide grains and transporting silver ions from smaller grains to bigger ones, thus contributing to increased visual acutance, but simultaneously to undesired graininess. In color reversal film, and also in black-and-white reversal development, inorganic thiocyanate as an additive to the "first developer" helps to establish the desired low level of "reversal fog".

### 3.1.1. Development Activators

The best means to activate silver development is to increase the availability of silver ions. Consequently, this is effected by adding complexing agents capable of transporting silver ions. Black-and-white photographers of earlier decades knew very well that the addition of small amounts of fixer to a developer leads to undesired results such as "dichroitic fog", mainly by loss of filament structure and consequently also of covering power of developed silver. In processing of color photographic materials where image silver is removed by the bleaching process, effects of this kind remain unobserved and it may be favorable to activate silver halide development in layers next to the film base where the alkaline developer arrives latest, most depleted and most contaminated by halide ions from the higher layers.

As a helpful means for activating preferably the development of lower layers in a photographic material, polymeric thioethers may be added. It is assumed that these polymers mainly influence the transport of silver ions.

Among low molecular thioethers, 3,6-dithiaoctane-1,8-diol **1** (Fig. 1) shows outstanding efficiency as a development accelerator, as a fixer and as a fogging agent as well. Compound **1** is used in the color developer solution of the E6-process for reversal film, where strong activation is needed to develop the chemically fogged emulsion grains left over. The use of **1** makes sense, as most of the iodide released during first development is consumed by conversion of residual grains lowering their development response. The fixing capability of **1** is helpful by providing silver ions for enhanced physical development, thus compensating for the reduced developability.

As another means for activating silver halide development by complexing silver, thiol-substituted carboxylic acids such as 3-mercaptopropionic acid or thiol-substituted alcohols such as thioglycerol which are released from Bleach-Accelerator-Releasing (BAR) couplers are most efficient.

In fact, BAR-couplers may be regarded as a kind of multipurpose tool, providing either activation of physical development and/or increased bleaching efficiency.

Water soluble mesoionic triazolium thiolates [40] such as **43** (Fig. 10) are powerful fixing agents and may be used both as development activators and bleach activators, due to the presence of a stable thiolate group and a pronounced hydrophilic character.

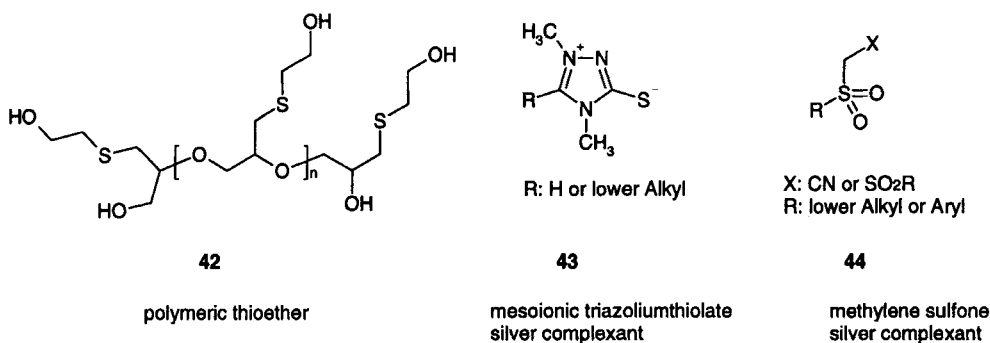


FIGURE 10 Development accelerators.

Methylene-*bis*-sulfones and cyanomethyl sulfones **44** have to be mentioned as another class of organic fixants, although the role of their higher-valent and electrophilic sulfur atom consists in providing an acidic  $\alpha$ -carbon which forms silver complexes [41]. This interpretation neglects the role of oxidized color developer, and it can be shown that the respective carbanions are capable of reacting slowly with the oxidised color developer, possibly by coupling, thus taking a less direct influence on silver halide development.

### 3.1.2. Development Inhibitors

In the development of color film, large amounts of inhibiting bromide or iodide are released. Why induce additional inhibition of development? The simple answer is that the inhibition of silver halide development, if spatially controlled, provides unique possibilities for improving photographic quality in color development, with respect to

- granularity,
- edge reproduction and suppression of color seams,
- color reproduction.

Since this matter will be discussed under the topic of DIR-couplers (Section 4), a discussion of development inhibition by heterocyclic thiolates such as the anions of 1-substituted 5-mercaptotetrazoles **45** or 2-mercapto-5-alkylthio-1,3,4-thiadiazoles **46** can be restricted to the mechanism by which it might be operating.

Inhibition of development appears to be caused by adsorption of the reagent to the AgX-microcrystal. On the other hand, it has been demonstrated that inhibition of development is caused by adsorption of development inhibitor to the growing silver filament. To make sure the inhibitors' point of attack, one has to consider that electron capture by latent image centra is highly preferred to electron injection at other places on the surface of a silver halide grain, mainly because electron injection is not an efficient process.

In principle, any polarizable organic anion (Fig. 11) such as **45** to **49** adsorbed on silver clusters forming the latent image should be capable of inhibiting the passage of electrons and lead to a delay in growth to the critical size where growth of the silver filament becomes explosive. Once this *induction period* has been overcome, even high concentrations of development inhibitor can be expected to have a small effect on

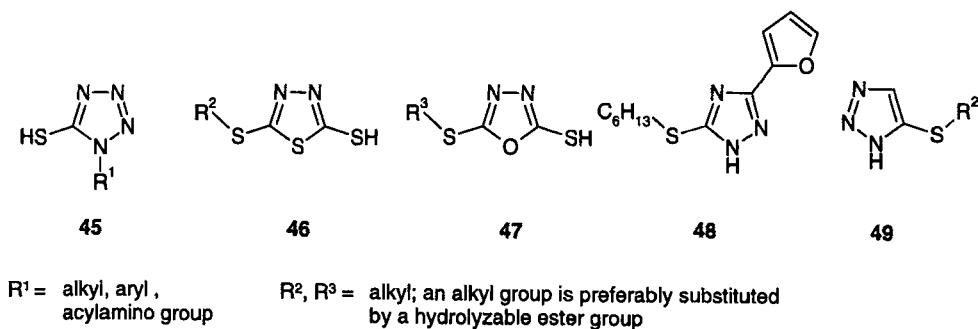


FIGURE 11 Development inhibitors (heterocyclic thiol or thioether).

the development of a silver halide grain, because the rapid growth of the silver filament overrides inhibition.

It has been shown that strong inhibition leads to the formation of truncated silver filaments. This may be put down to the fact that increased local concentration of bromide or iodide from neighbouring grains lead to a low concentration of interstitial silver ions within the emulsion grain, and consequently a low supply.

Certainly, adsorption of a development inhibitor at trivial positions of the grain surface lowers the concentration of interstitial silver ions at the grain surface. The phenomena involved are not trivial, however. It is poorly understood why certain development inhibitors decrease the photographic speed of an emulsion layer while others lead to a lowered maximum density and a lower slope ( $\gamma$ -value) of the characteristic curve.

### 3.1.3. Sulfur-Containing Nucleophiles in Color Development

In color development, the presence of strong sulfur nucleophiles such as aliphatic thiolates leads to loss of coupling efficiency, and therefore, even the use of sodium sulfite or sodium benzenesulfinate is restricted to low concentrations. In experiments by cyclic voltammetry, sulfinates can be shown to react very sluggishly with oxidized color developer, with the result that current-potential curves of color developers such as CD-4 show no apparent change when sulfinate is present. This kind of inert behaviour may not apply to the silver halide emulsion itself, which is sensitive to the presence of nucleophilic sulfur compounds. It is commonly accepted that sulfinate ions are capable of adding to the terminal nitrogen of quinone diimine in exactly the same way as a coupler anion, with the formation of N-sulfonylated color developer **50** (Fig. 12).

Disulfides are in general not reduced by the color developer, in much the same way as heterocyclic thiols such as the mercaptotetrazoles are normally resistant to oxidation by color developer oxidation product. The difference in redox potentials is at least +300 mV. As a target of photographic research, activation of color development, e.g. by nucleophilic sulfur compounds, has always been attractive enough to justify careful investigation. In practice, however, few color development activators have been found worthy of introduction into industrial products, mainly for reasons of enhanced fog.

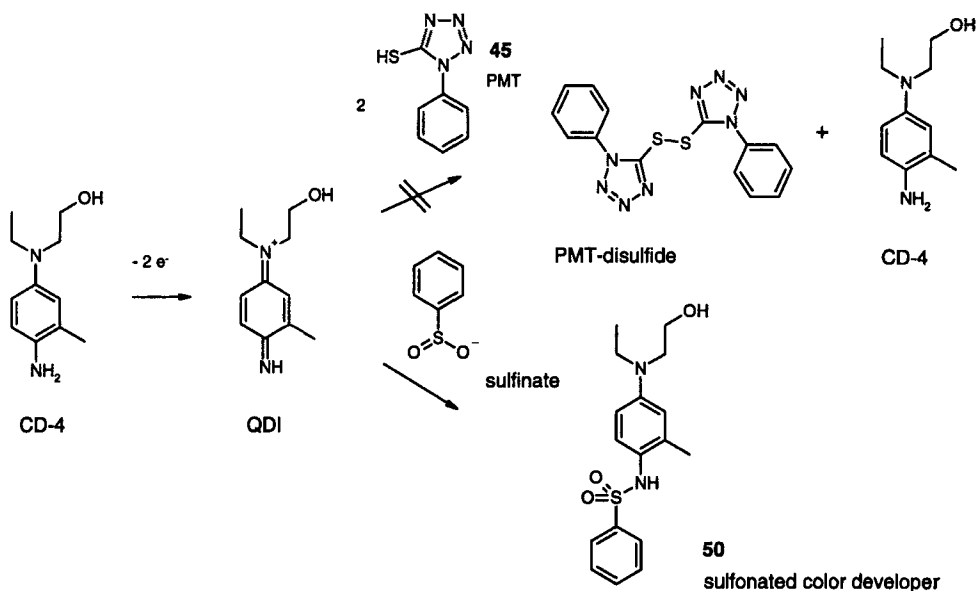


FIGURE 12 Sulfur-containing nucleophiles in color development.

### 3.1.4. Developers Containing Sulfur

Mono- and disubstituted hydroquinones are capable of adding sulfite, sulfinate, and even more thiolate ions when they are oxidized under photographic conditions. The resulting substituted hydroquinone species are still regarded as developers, although of higher oxidation potential and consequently of lower value. It has been claimed that hydroquinone derivatives or derivatives of gallic acid containing heterocyclic thiol moieties such as a 1-substituted mercaptotetrazole or a mercapto-oxadiazole moiety may be used as stabilizers, to protect photographic material against pressure-induced sensitization [42]. Ballasted hydroquinones or similar developer moieties containing a 1-substituted mercaptotetrazole or a similar heterocyclic thiol as a substituent, which can be split off by oxidation under development conditions, have turned out as a valuable tool for increasing acutance and color saturation in color reversal film by controlled inhibition of first development. However, it has also been demonstrated that the heterocyclic thiol is readily released by the sulfite present in the developer [43].

### 3.2. Organic Sulfur Compounds in Silver Bleaching and Fixation

In ordinary black-and-white photography and in radiographic material or graphic film, the picture is made up of silver, due to its high covering power and permanence. By contrast, in color photography silver is formed only as an undesired by-product of dye formation which has to be removed by an extra processing step. This is done by “bleaches” or “blixes” or “bleachfixers”, i.e., processing solutions containing oxidants capable of either rehalogenating or directly transforming image silver into soluble silver complexes (see Fig. 13).

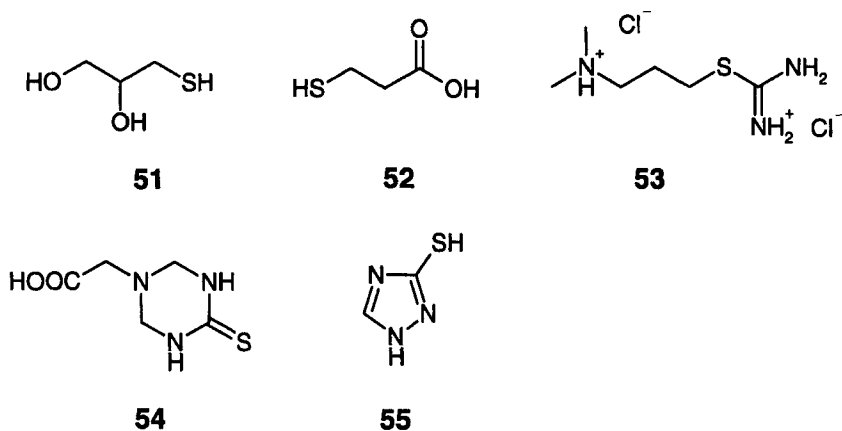


FIGURE 13 Bleach accelerators and "blix" accelerators.

### 3.2.1. Bleach Activators

Moderately stable organic complexes of Fe(III), especially those with persubstituted amino-polycarboxylic acids or diamine-tetra-alkanoic acids such as EDTA have been used as the oxidants in the most favorable kind of bleach, especially under the aspect of simple processing and ecological compatibility. Other bleaching agents such as potassium hexacyanoferrate(III) or potassium peroxydisulfate are in marginal use.

**3.2.1.1. Thiol/Disulfide Bleach Activators** Under unfavorable conditions, especially under conditions of strong exhaustion when the proportion of Fe(III) to Fe(II) is low, the activity of a bleach fixer solution may decrease to a level where the developed material retains silver, first recognized in high-density areas where the color becomes dull.

To extend the range of acceptable print quality, bleach-activating additives are used, mainly of the thiol or thiol-precursor type. Thiols such as thioglycerol **51** and mercaptocarboxylic acids such as **52** are very useful and show a residual efficiency even when feebly oxidized. Preferably, thiol type bleach accelerators are applied via a conditioner solution where the bleach accelerator is inaccessible to the oxidizing power of the bleaching agent. Apart from hydroxyalkanethiols, suitable thiol/disulfide bleach accelerators [44] are also found in the substituted amino-alkanethiol classes. It is not clear to what extent the bleach-activation is caused by air-induced reoxidation of an Fe(II) complex, containing a thiol ligand. The thiocyanate ion, a valuable inorganic bleach accelerator, is well known for its strong capability to form Fe(III) complexes.

**3.2.1.2. Isothiuronium Salts** As precursors for bleach-activating thiols, which in the presence of the bleaching agent are unstable over longer periods of time and have to be fed into the system by increased regeneration rates, isothiuronium salts **53** have also been claimed. Again, their efficiency may be based on slow hydrolysis to free thiols as the actually efficient bleach accelerators.

**3.2.1.3. Thioethers as Bleach Activators** The use of polymeric thioethers of the polyglycidyl-sulfide type such as **42** as bleach accelerators for bleaches based on

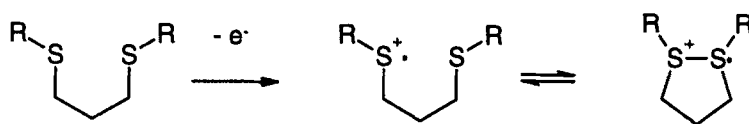


FIGURE 14 Single-electron transfer to oxidant.

hexacyanoferrate(III) has been claimed, especially for reversal processing. Bleaches containing this unusual combination of hydrophilic thioether polymer and potassium hexacyanoferrate(III) as the oxidant have been used in an abandoned process for developing super-8 film [45].

The chemical reactions by which thioethers may assist in the bleaching of silver halide are basically unknown. Recent investigations have shown that in the oxidation of *bis*-thioethers whose sulfur atoms are separated by one to four aliphatic carbon atoms, an absorption in the visible spectrum can be observed, corresponding to a cyclic radical cation intermediate in its electrochemical behavior [46]. The unusual *S,S*-three-electron bond is stabilized by a preferably five-membered ring. Further oxidation yields a dication which is readily hydrolyzed to a mono-sulfoxide (Fig. 14).

### 3.2.2. Activators for use in Bleach-Fixing Solutions

At first sight, combining thiosulfate as a fixing agent and an Fe(III) chelate such as Fe(III)EDTA in a processing solution designed for long-time use does not seem promising. In fact, stable "blix"-solutions based on this composition have been in use for at least forty years. They were initially designed for processing color paper based on silver bromide emulsions. The replacement of silver bromide by silver chloride in the present color paper system has further increased the performance and safety of the process, apart from situations where the use of novel sensitizing dyes or novel stabilizers might create problems.

The use of 3-mercapto-1,2,4-triazole **55** (Fig. 13) as a bleach accelerator has been well known for improving processing reliability. Certain earlier disclosures [47] claim the use of heterocyclic thiones as bleach accelerators in general. More efficient bleach accelerators such as 5-alkylhexahydro-1,3,5-triazine-2-thiones **54** [48], isothiuronium salts containing additional amino groups **53** [49] and 1,4,5-trisubstituted 1,2,4-triazolium-3-thiolates **43** (Fig. 10) have been claimed [50], but apparently not entered commercial use.

While the efficiency of all other types of bleach accelerators is lost under conditions of prolonged use, the mesoionic triazolium-thiolates such as **43** are found to be stable in contact with the bleaching reagent and their use does not depend on increased regeneration rates.

### 3.2.3. Bleach Inhibitors

1-Phenyl-5-mercaptotetrazole (PMT", R<sup>1</sup>=Phenyl) has turned out to be one of the most powerful bleach-inhibiting substances, and consequently it has been used occasionally for intentional protection of image silver against bleaching, for example in IR-readable soundtracks of some older type movie film. The necessarily high amounts of PMT (**45**) were provided by a DIR-coupler combined with an infra-red-sensitized emulsion.

### 3.2.4. Sulfur-Containing Organic Fixants

Among organic fixants 5-substituted hexahydro-1,3,5-triazine-2-thiones **54** and 1,4,5-trisubstituted 1,2,4-triazoliumthiolates **43** deserve mentioning, but their use may be restricted to very few cases where ammonium thiosulfate cannot be used.

## 3.3. Organic Sulfur Compounds for Post-Treatment of Photographic Images

### 3.3.1. Stabilization of Silver Images by Bunte-Salts

The silver image obtained in the development of certain printing materials has been shown to undergo rapid oxidation in the presence of noxious components of the atmosphere, especially in closed rooms and in the presence of traces of hydrogen peroxide. It has been shown that the addition of alkali thiocyanates or S-alkyl thiosulfates (Bunte salts) protects the highly dispersed image silver. Under unfavorable conditions however, all image-silver protecting agents based on sulfur have proved inferior to 3-amino-1,2,4-triazole as an image silver-protecting agent.

### 3.3.2. Toning of Silver Images by Heterocyclic Sulfur Compounds

The toning of silver images by development in the presence of heterocyclic thiols as toning agents may be regarded as a subject of mainly historical interest. It may prove interesting where the adsorption of certain surface-modifying agents actually leads to a silver surface showing an entirely different character. The use of certain 2-mercapto-1,3,4-oxadiazoles **47** (Fig. 11) bearing bulky hydrophobic residues  $R^2$  as development inhibitors has facilitated the manufacture of directly accessible printing plates where the developed silver image is hydrophobized to such a high degree that it can be used as the ink-receiving element in offset printing plates.

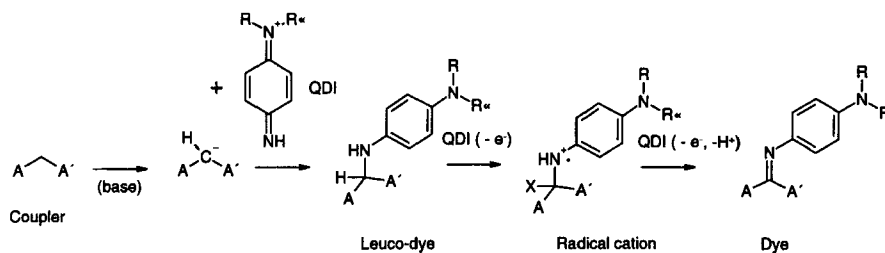
## 4. ORGANIC SULFUR COMPOUNDS IN SYNTHESSES OF COUPLERS FOR COLOR PHOTOGRAPHY

The chemistry of chromogenic materials, film as well as printing material, is centered about the process of *color formation* by chromogenic coupling. Sulfur compounds are used either as tools for modifying the process of image formation or as building blocks of couplers, to improve processing and image quality. A particular aspect deals with temporarily electrophilic sulfur.

As the first step of color formation, oxidation of color developer (e.g. CD-4) takes place and quinone diimine (QDI) is formed within the "oxidized color developer" (Fig. 15). Chromogenic coupling between an active methylene or methine compound (coupler) and QDI as the *N*-electrophile proceeds as a multi-step reaction, by addition of the coupler anion to the terminal nitrogen of the quinone diimine QDI, and primarily leads to a leuco compound which still exhibits the characteristics of a developer. It has to be oxidized by additional QDI to yield an azomethine dye. Thus, the overall transformation of coupler into azomethine dye turns out to be the result of four-electron transfer from color developer to silver halide: four silver ions are reduced to metallic silver to form one molecule of dye. The silver demand may be considerably higher when the radical cation intermediate formed in the first step of leuco-dye oxidation

**Four-Equivalent Coupling**

(A, A' = electron accepting, e.g. acyl or carbonamide groups)

**Two-Equivalent Coupling**

X = nucleophilic leaving group, e.g. thiol RS-

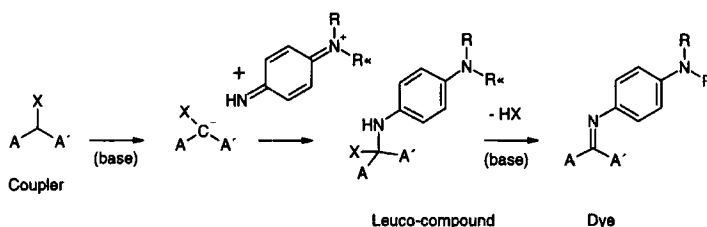


FIGURE 15 Chromogenic coupling.

has a tendency to decay.<sup>1</sup> This reaction sequence is commonly known as *four-equivalent coupling*.

Dye formation can be transformed into a more efficient and less silver consuming process known as *two-equivalent coupling*, by substituting the coupling position with a nucleophilic group X such as a halogen atom, a phenoxy group, an alkoxy group, an imide or hydantoin group, an azole heterocyclic group or a sulfur atom linked to an aliphatic, aromatic or heterocyclic residue, which essentially determines the reactivity of the thiol leaving group in the photographic system.

The electron-accepting character of the nucleophilic substituents and steric requirements exhibit a powerful, although *a priori* unpredictable, influence on the reactivity of a nucleophile-substituted coupler. Once it undergoes coupling with quinone diimine the intermediate leuco compound is no more dependent on further oxidation because it can split off the leaving substituent by base-induced  $\beta$ -elimination. Thus, only two equivalents of silver are consumed instead of at least four, and couplers bearing a nucleophilic leaving group are commonly classified as *two-equivalent couplers*.

#### 4.1. Syntheses of Pyrazolo[5,1-*c*](1,2,4)Triazole Couplers by Sulfur Extrusion from Thiadiazines

Among different classes of magenta couplers, the pyrazolo [5,1-*c*](1,2,4)triazoles [51] and the pyrazolo[1,5-*b*](1,2,4)triazoles [52] have been introduced primarily for printing

<sup>1</sup>Evidence for this process, leading to reduced dye yield, was presented at IS&T's PICS Conference, Portland, May 17–20 1998 Paper 36C-P117 (P. Berghaller, U. Nickel, *Some unexpected observations in cyclo-voltammetric investigations of chromogenic coupling*); *Chem. Abstr.* 131:279149 (1999).



materials, and with the aim of improving image quality.<sup>2</sup> The hues of the azomethine dyes are superior to those obtained from pyrazolone couplers, the stabilities of the dyes are acceptable to excellent, and residual coupler in white areas of the image is stable enough to yield no color stain problems.

In general, the reactivity of pyrazolotriazoles is inferior to that of pyrazolones which are used mainly in color negative and color reversal film. To increase the daylight stability of azomethine dyes from pyrazolo[5,1-*c*](1,2,4)triazole type couplers, and to a minor degree from pyrazolo[1,5-*b*](1,2,4)triazoles as well, the couplers are substituted by a bulky *tert*-butyl substituent in the 6-position of the bicyclic system [53,54]. A reduction in coupling activity is accepted, but the substituent yields some synthetic problems<sup>3</sup> which have been overcome by a synthesis based on sulfur extrusion [55] from triazolo[3,4-*b*](1,3,4)thiadiazine intermediates [56].

The reaction sequence upon which this synthesis is based starts with the condensation of thiocarbohydrazide and chloropinacolone to form the 2-hydrazino-1,3,4-thiadiazine intermediate (Fig. 16). Once this has been acylated to give **56** and cyclized to the 1,2,4-triazolo[3,4-*b*](1,3,4)thiadiazine **57** by refluxing **56** in an inert solvent such as acetonitrile it is *N*-acylated in acetic anhydride. On further heating, the acylated intermediate **58** undergoes desulfurization to a pyrazolo[5,1-*c*](1,2,4)triazole which is deacylated to form e.g. the chlorinated derivative **59**. The synthesis may be conducted either with direct removal of the sulfur atom after the cyclization step, or in a different way where the sulfur atom is preserved for later use as a part of a leaving group.

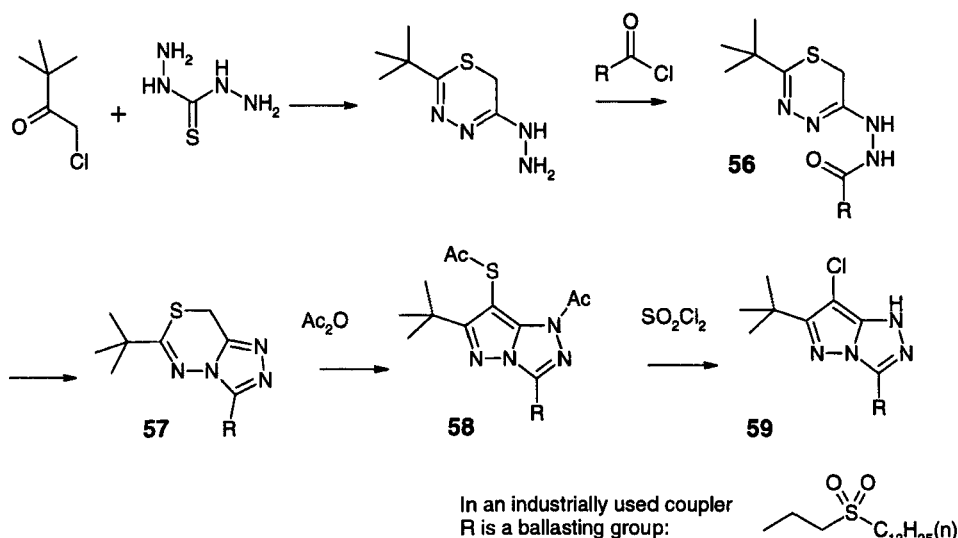


FIGURE 16 Synthesis of a pyrazolo[5,1-*c*](1,2,4)triazole coupler via a sulfur extrusion step.

<sup>2</sup>Pyrazolo[1,5-*b*](1,2,4)triazoles are not discussed within this article.

<sup>3</sup>An earlier synthesis was based on the preparation of 3-*tert*-butyl-5-hydrazinopyrazol, its acylation and cyclization by phosphoryl chloride.

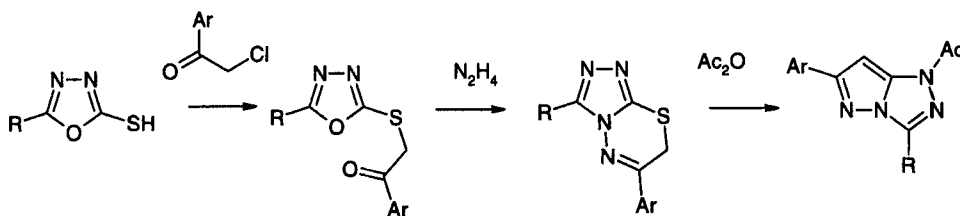


FIGURE 17 Pyrazolo[5,1-*c*](1,2,4)triazoles via sulfur extrusion: synthesis avoiding use of thiocarbohydrazide.

Since thiocarbohydrazide is classified as an explosive, technical syntheses may be carried out advantageously along different pathways such as one described in its first steps by Krasnovskii [57], where the 1,2,4-triazolo[3,4-*b*](1,3,4)thiadiazine is obtained by hydrazinolysis of an oxidazole ring (Fig. 17). A problem common to pyrazolo[5,1-*c*](1,2,4)triazole syntheses via a desulfurization step is the removal of sulfur-containing contaminants which lead to reduced photographic speed. Smooth desulfurization is achieved either by means of sulfuryl chloride such as in the synthesis of **59** or by sulfur-accepting phosphorus(III) compounds such as hypophosphorous acid [58], where a four-equivalent coupler is obtained. To some degree, the sequence of synthesis steps can be varied.

## 4.2. DIR-Couplers and Related Compounds [59]

### 4.2.1. Photographically Active thiol groups: Linking Photographically Useful Groups via Electrophilic Sulfur

Among the manifold applications of sulfur compounds in coupler chemistry, the use of sulfur as a "building element" in two-equivalent coupler chemistry appears most important.

In general, a thiol group occupying the coupling position increases the acidic character of the coupler. This may lead either to enhanced coupling reactivity due to a higher degree of deprotonation, if the respective four-equivalent coupler shows low acidity as it is known from pyrazolo[5,1-*c*](1,2,4)triazole four-equivalent couplers, or to reduced coupling reactivity, if the acidity of the four-equivalent coupler is high. While an electron-accepting substituent such as a heterocyclic thiol reduces the initial reactivity of the coupler, it may be helpful in performing the final transformation of the intermediate to the azomethine dye. Thus, there is no basis for safe predictions on coupling rates of two-equivalent couplers.

The principle of inhibitor-induced activation to coupling is readily understood by comparing acetophenone, which does not give the coupling reaction, and 1-phenyl-5-phenacylthio-tetrazole **60**, which shows all characteristics of a DIR-coupler [60]. Additional activation results from attachment of the phenylmercaptotetrazol (PMT)-group **45** to a cyclic system such as that of DIR-indanones **61** (Fig. 18).

Apart from their influence on coupling activity, many thiol groups have proved to be literally "photographically useful". Some aliphatic thiols such as thioglycerol, cysteine and 3-mercaptopropionic acid are capable of activating silver development and also silver bleaching by forming soluble silver complexes, and have therefore gained technical importance as constituents of "Bleach-Accelerator-Releasing Couplers"

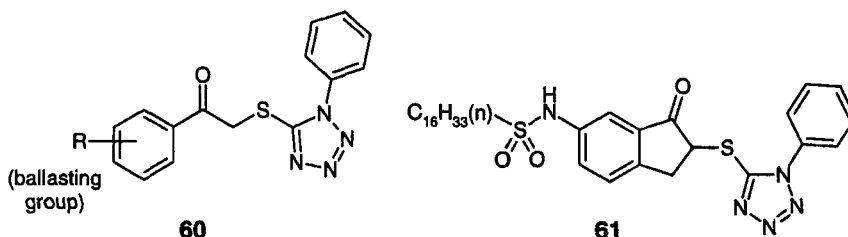


FIGURE 18 DIR-couplers of the phenacyl-PMT type.

Cyan couplers releasing photographically useful groups PUG

DIR-coupler, DIAR-coupler, BAR-coupler:  
 photographically useful thiol compounds are split off  
 - either directly as a leaving group  
 - or from a timing group

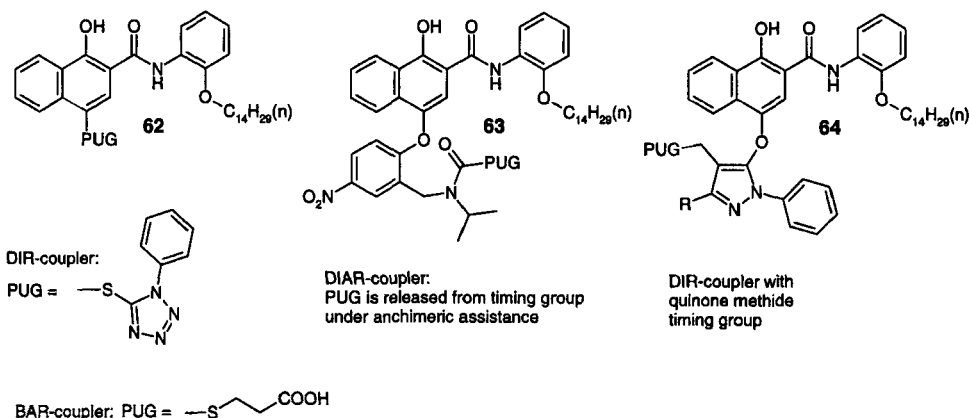


FIGURE 19 Cyan couplers releasing photographically useful groups PUG.

(BAR-couplers) [61], or “Soluble Mercaptan Releasing Couplers” (SMR-couplers) [62]. Couplers capable of releasing a development inhibitor group in the course of color development have been called DIR-couplers (Development Inhibitor Releasing Couplers). DIR-couplers (Fig. 19) have played an important role in the design of high-definition color film for about 25 years.

During development of a photographic layer containing DIR-couplers, development inhibitors, e.g. heterocyclic thiols such as 1-alkyl-5-mercaptotetrazoles and 1-aryl-5-mercaptotetrazoles **45** or 2-mercapto-1,3,4-thiadiazoles **46** (Fig. 11), are released from the coupling position of the DIR-coupler and adsorbed by the growing silver filaments of emulsion grains.

- If a sufficiently acidic thiol group, such as that of 1-phenyl-5-mercaptotetrazole (PMT), is strongly adsorbed to developing silver halide, it does not diffuse very far from the developing grain. This inhibits the development of only a few grains in the close neighbourhood of the developing grain and leads predominantly to an improvement in granularity.
- If the adsorption of the thiol group to silver is weaker, such as that of 1-alkyl-5-mercaptotetrazoles **45**, its diffusibility consequently turns out higher, and it may

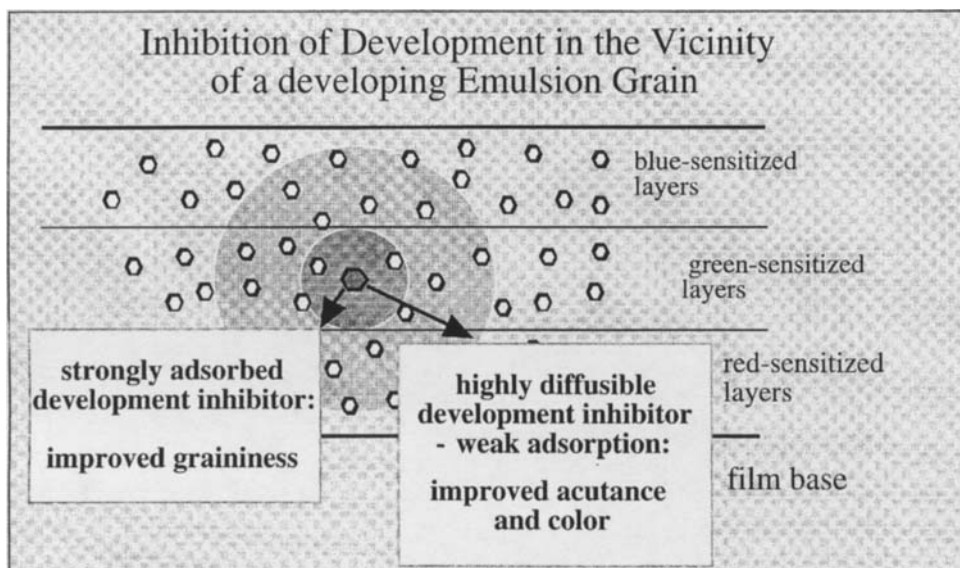


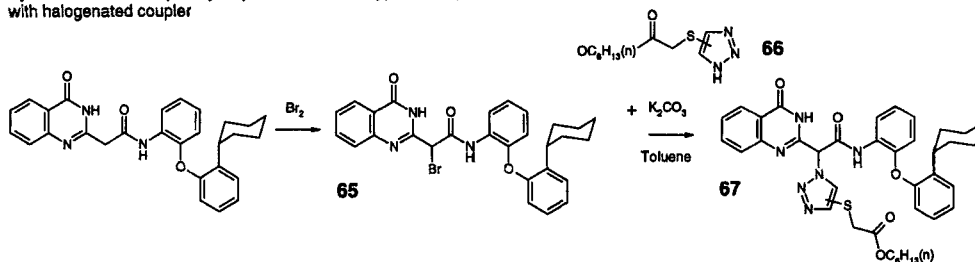
FIGURE 20 Inhibition of development in the vicinity of a developing emulsion grain.

exert a weaker inhibition on silver halide grains accessible over larger distances, which leads to photographically useful long-range effects. “Edge effects” and “inter-layer interimage effects” are highly desirable with regard to edge reproduction and improved color saturation which increases by restrained dye formation in adjacent layers where dyes of a different color are formed (Fig. 20).

The number of patents covering the use of DIR-couplers in color negative film appears tremendous [63]. Structure **62** (Fig. 19) exemplifies the older type of DIR-coupler where the development inhibitor is linked to the coupling position without a spacer or “timing” group. A major part of DIR-couplers disclosed after 1980 contains a timing group as the primary leaving group, which after being split off releases the development inhibitor group itself by a consecutive reaction, e.g. of the intramolecular nucleophilic displacement type. DIR-couplers such as **63** and **64** containing a development inhibiting moiety linked to the coupler by a reactive spacer group have been developed for different reasons, mainly to optimize coupler reactivity and diffusion range of the inhibitor. If the leaving group is capable of splitting off the development inhibitor by cyclization, i.e. under anchimeric assistance, the couplers are classified as Development-Inhibitor-Anchimeric-Release Couplers (DIAR-couplers) [64]. Other mechanisms by which a development inhibitor moiety is released from a primary leaving group remain outside the scope of this article.

The electrophilic chemistry of thiol groups under “*Umpolung*” provides efficient methods for directly linking thiols to a coupler. In bench scale syntheses of DIR-couplers, heterocyclic thiols of high acidity, e.g. the mercaptotetrazoles **45**, are either oxidized to disulfides sufficiently electrophilic to provide transfer of one thiol group to a nucleophilic coupler, or they are treated with an oxidizing or chlorinating agent, e.g. sulfur chloride, whereby the thiol undergoes selective chlorination to a sulfonyl chloride **68** which attacks the four-equivalent coupler **69** (Fig. 21). In another synthesis

Synthesis of DIR-Coupler by alkylation of triazole type development inhibitor with halogenated coupler



Synthesis of DIR-coupler by sulfenylation of four-equivalent coupler with sulfonylchloride, derived from heterocyclic thiol type inhibitor

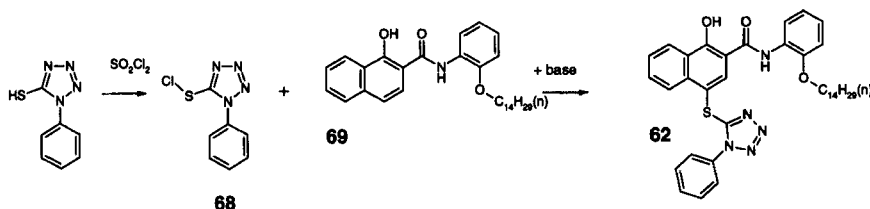


FIGURE 21 Synthesis of DIR-coupler.

of technical importance, a mixture of coupler and thiol are oxidized *in situ*. In still another method, the thiol is oxidized separately to a derivative of the sulfenic acid, e.g. a sulfonyl imide, which is then added to a mixture of coupler and auxiliary base.

The concept of linking halogenated, i.e. electrophilic couplers, to thiolate nucleophiles has proved less attractive, since most couplers accessible by this method show low reactivity. On the other hand, strongly nucleophilic thiolates are capable of reducing halogen-substituted, especially brominated couplers **65** to the four-equivalent couplers.

This may apply in particular to DIR-couplers bearing a yellow coupler moiety of the acylacetoanilide or malonanilide type or a similar hetaryl acetoanilide coupler. Highly efficient DIR-couplers of the quinazolinone-2-acetanilide type [65] such as **67** (Fig. 21) contain 1,2,3-triazoles **66** or 1,2,4-triazoles as development inhibitors of choice, which have a low tendency to diminish the reactivity of the coupler moiety in general, show good inhibiting power and carefully balanced diffusibility, controlled essentially by a thioether substituent. As a chemical moiety, the thioether group of **66** is not involved in the substitution reaction. It just increases the acidic character of the triazole species, and consequently modifies its inhibiting power.

Attempts to find out what actually happens when a strongly nucleophilic thiolate group reacts with oxidized color developer have led to open questions. The subject has apparently not been investigated in detail and with any clear results. Certainly, thiolate can function as a kind of QDI-trap capable of binding quinone diimine which may be released later, and possibly under post processing conditions.

Evidence from experiments under TLC-conditions shows that the violet color reaction of the Wurster-type between color developer and neutral oxidant is rapidly quenched by thiols and replaced by a stable yellowish to orange color which depends on the thiol substituent and whose nature is unknown.

It is not really known how thiol-type development inhibitors react with silver halide as the oxidant, in particular with the silver filament functioning as the anode of the

grain: thiolate groups of typical inhibitors might be capable of “sealing” the active surface by a chemical reaction forming electrochemically neutral disulfide as a dielectric barrier reducing the passage of electrons from developer to silver halide.

#### 4.2.2. Photographically Inert Thiol Leaving Groups

Ballasted arenethiols showing low diffusibility have been used in a different type of two-equivalent magenta coupler for color negative film introduced since 1992. The novel 3-anilinopyrazolones make use of nearly inert arenethiol groups. Most magenta couplers of this kind (Fig. 22, e.g. **71**) are derived from the four-equivalent 3-anilinopyrazolone **70** which has been used as a magenta coupler in color paper for many years [66].

The main features of the arenethiol-substituted type of two-equivalent coupler are high dye yield, high coupling reactivity and high intrinsic stability. Couplers such as **71** are readily prepared from **70** and an electrophilic precursor of the leaving group, e.g. a sulfonyl chloride or bromide.

The primary function of the sulfur atom in these couplers consists in reducing the silver demand for dye formation and stabilizing the coupler to attack by aldehydes. The thiol substituent has been preferred to other nucleophilic groups for one reason: no other kind of leaving group is available without additional problems, chemical or photographic, and at lower cost.

As a drawback of some importance, some examples of thioether-substituted anilino-pyrazolone magenta couplers **71** have been biased for post-process density increase. This phenomenon has been attributed to delayed coupling or delayed release of the leaving group and remedied by incorporation of non-coupling aromatic amines or heterocyclic bases as “density stabilizers”.

Electrochemical measurement of the relative coupling rates of coupler dispersions shows that addition of a weakly basic “density increase restrainer” leads to a coupling rate approximately twice as high as that of the reference dispersion.<sup>4</sup> Thus, it may be doubted if weak organic bases are actually capable of preventing post-process-density increase. What a basic additive could actually induce is an increase in escape rate of the thiolate anion in the dye-forming step.

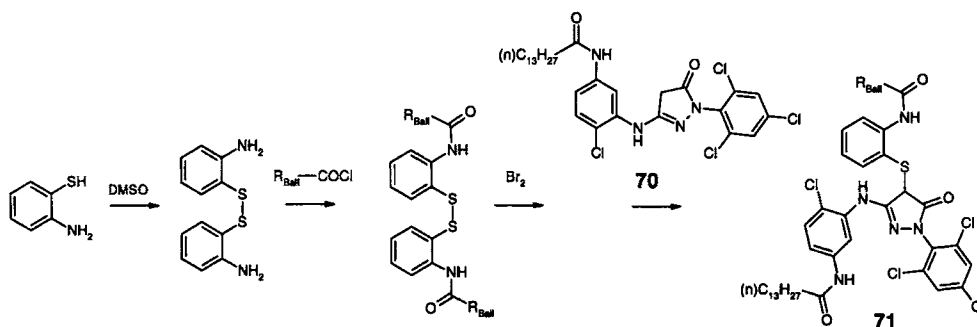


FIGURE 22 Synthesis of magenta two-equivalent coupler.

### 4.3. Use of Sulfur as an Auxiliary Electrophilic Group in Two-Equivalent Coupler Synthesis

#### 4.3.1. The Sulfurane Contraction

A more sophisticated kind of two-equivalent coupler synthesis has been found in the course of experiments designed to synthesize DIR-couplers bearing a triazole or benzotriazole type development inhibitor as the leaving group of an anilinopyrazolone, such as **72**. Attempts to achieve monobromination of an acyl-protected anilinopyrazolone and to substitute the 4-bromine atom by **72** as the substituent had failed, but experiments carried out with selenium dioxide instead of bromine were actually found to deliver the desired DIR-coupler **73** in moderate yields (20–35% of the theoretical) and as a mixture of two isomers (Fig. 23) [67].

To avoid the use of toxic selenium-containing intermediates, the novel synthetic strategy was applied to hypervalent sulfur(IV) intermediates, and it was found that the sulfur-analogue can be used with even higher versatility, although the sulfuranes are short-lived in general, comparable to diazonium salts. They were prepared mainly from the respective thio-*bis*-coupler **74** (from **69** and sulfur dichloride, Fig. 24) and further processed at temperatures preferably below 0°C. The best results were obtained at –20°C. Above 0°C, a C,C-dimerization reaction can be shown to dominate the complex reaction pattern, most probably induced by a tendency to ligand coupling.

The novel arylation reaction [68] was readily applied to a selection of couplers and acidic azoles, preferably of the 1,2,3-triazole and benzotriazole series (**66**, **72** and others). The most favorable results were obtained within the 1-naphthol-2-carbonanilide cyan coupler series where stable DIR-couplers such as **75** were obtained in yields up to 65% of the theoretical. The position of the thioether group on the 1,2,3-triazole ring was not determined beyond doubt. Compound **75** was found to be a DIR-coupler of outstanding efficiency. Fair results have been obtained in the pyrazolo[5,1-*c*](1,2,4)triazole series. On the other hand, most of the triazole-substituted two-equivalent couplers of the anilinopyrazolone class were shown to be unstable.

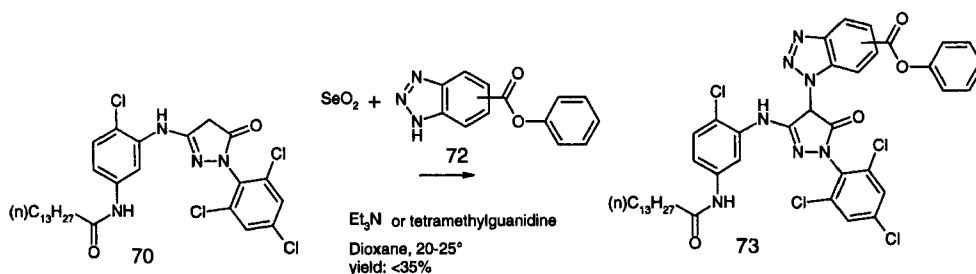


FIGURE 23 Synthesis of anilinopyrazolone type DIR-coupler via selenurane intermediate.

<sup>4</sup>P. Bergthaller / Agfa-Gevaert, U. Nickel, K. Bauer, both University of Erlangen-Nürnberg: unpublished measurements by cyclic voltammetry of CD-4 in the presence of coupler dispersions; we used a branched 2-tricythio-benzimidazole as the density stabilizer.

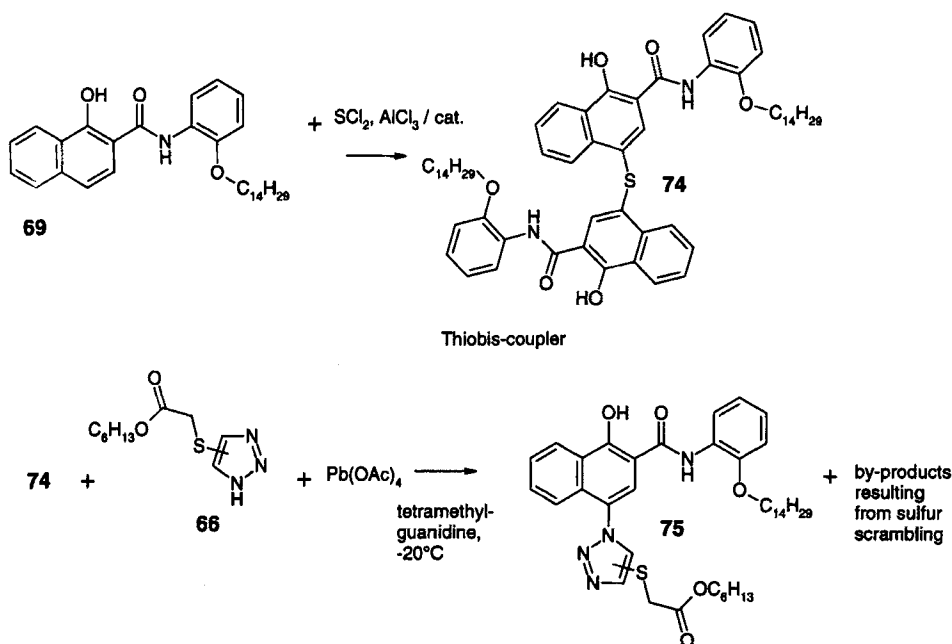


FIGURE 24 Synthesis of naphtholcarboxanilide type DIR-coupler via sulfurane contraction.

The preferred method of synthesizing appropriate tetravalent sulfurane intermediates consists in treating a thio-*bis*-coupler **74**, preferably in dichloromethane or trichloroethene as the solvents, with lead(IV) acetate or certain chlorinating agents such as *N*-chlorobenzotriazole, *N*-chlorosaccharine and *N*-chlorosuccinimide, and inducing ligand exchange by adding successively the 1H-triazole derivative, e.g. **66**, and tetramethylguanidine, with the consequence of rapid collapse of the intermediate sulfurane. The use of even small amounts of protic or strongly coordinating solvents such as ethanol, tetrahydrofuran, pyridine or acetonitrile has to be avoided, and traces of acetic acid were removed from lead tetraacetate. The presence of a thioether group in **66** leads to a somewhat reduced yield of two-equivalent coupler, due to competing oxidation of the thioether group.

Under conditions of kinetic control, 1,2,3-triazoles are linked to the coupling position preferably by their 1- or 3-nitrogen atoms. Interpretation of NMR-spectra does not give clear indications as to which position is actually involved. Contrary to other types of direct nucleophilic substitution where mixtures of usually two isomers are formed, sulfurane contractions proceed with formation of preferably one isomer. This high selectivity, and a generally observed preference for the more acidic heterocyclic ligand, has been tentatively attributed to *thiophilic control*, where the stability of the ligand-sulfur bond appears to determine the sequence of the ligands leaving the collapsing sulfurane and the constitution of the final product.

The reaction has been also applied to benzotriazole as the substituent and a sulfinyl-*bis*-naphthol coupler instead of the thio-*bis*-naphthol derivative, under otherwise identical conditions and most probably by participation of a penta- or hexacoordinate, acetoxy-sulfurane(VI) intermediate which is formed by addition of lead(IV) acetate or



phenyliodo-*bis*-trifluoroacetate. However, this variety of sulfurane collapse appears to give only low yields of benzotriazole-substituted two-equivalent coupler.

#### 4.3.2. Pyrrolo[1,5-*b*](1,2,4)triazole Type Cyan Couplers: a Novel Synthesis via a Pummerer-like Intermediate

Pyrrolo[5,1-*c*](1,2,4)triazoles and pyrrolo[1,5-*b*](1,2,4)triazoles bearing electron accepting substituents in non-coupling positions (e.g. **81** in Fig. 25) have been disclosed as a new type of heterocyclic cyan coupler since 1990 [69]. Refinements in coupler structure and adequate choice of substituents have led to a novel class of cyan couplers capable of producing azomethine dyes with high color strength and clean red absorption. Procedures for their syntheses have been described in a series of patents between 1991 and 1997 [70].

Azomethine chromophores obtained by coupling of representative four-equivalent couplers showed high resistance to thermal fading while their resistance to actinic light needed improvement. On prolonged storage under conditions of high temperature or humidity, white areas showed a marked tendency to reddish stain, for which oxidation of residual four-equivalent coupler was blamed.

To study the shelf life of finished prints we were interested in pyrrolo[1,5-*b*](1,2,4)triazole type two-equivalent couplers bearing a thiophenol group in the 7-position and succeeded in synthesizing this type of coupler by a novel pyrrole ring closure based on a cycloalkylation step closely related to the Pummerer-reaction [71] (Fig. 25). The sulfur atom involved is an essential part of the target molecule.

Condensation of the triazole-3-acetate **76** with the unstable phenylthioacetaldehyde [72] in the presence of zinc chloride yields a 2-(triazole-3-yl)-(3-phenylthio)methacrylate

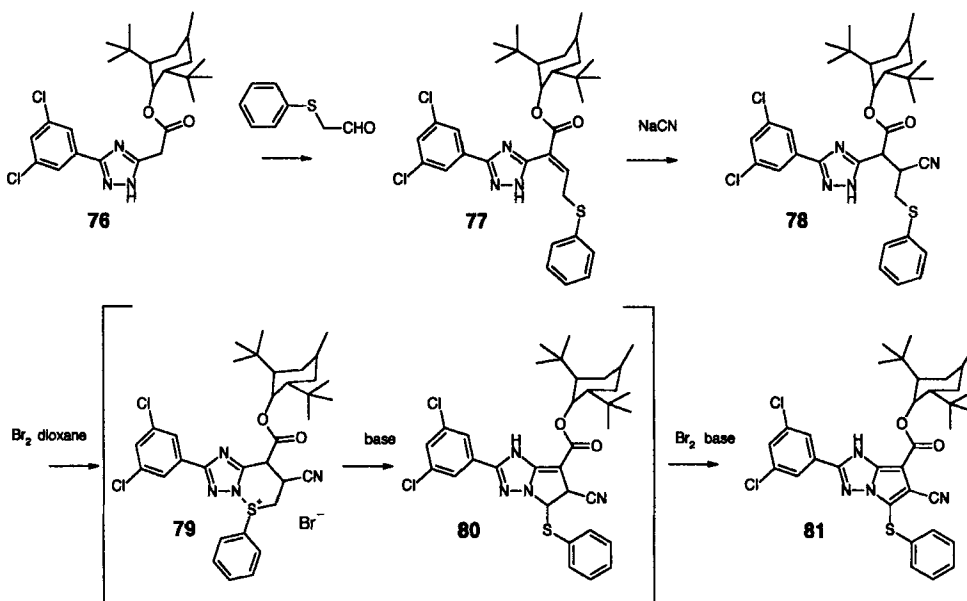


FIGURE 25 Synthesis of pyrrolo[1,5-*b*](1,2,4)triazole by a Pummerer-like cyclization.

intermediate **77** which adds HCN from a solution of sodium cyanide in *N,N*-dimethylacetamide to give **78** which can be isolated and characterized by  $^1\text{H}$ -NMR-data. Compound **78** is brominated with dioxane-bromine and immediately yields the strongly fluorescent and therefore easily identified pyrrolotriazole coupler **81**, either via an  $\alpha$ -bromosulfide intermediate **79** capable of undergoing cyclization or by direct attack of the triazole ring onto the electrophilic sulfur atom. Although a second equivalent of bromine is needed to achieve dehydrogenation of the hypothetical intermediate **80**, addition of bromine in amounts higher than one mol/mol of intermediate was found disadvantageous. The pyrrolotriazole coupler was isolated in yields not exceeding 20% of the theoretical.

Ambiguities about the regioselectivity of the cyclization step which might have delivered either the desired pyrrolo[1,5-*b*](1,2,4)triazole or an isomer pyrrolo[5,1-*c*](1,2,4)triazole were remedied by evaluation of NOE-difference-measurements of the  $^{13}\text{C}$ -NMR-spectra which made clear that **81** had the desired constitution of the pyrrolo[1,5-*b*](1,2,4)triazole derivative [73].

As a novel method for synthesizing anellated pyrrole derivatives [74], the new pyrrolotriazole synthesis via a Pummerer-type intermediate does not yield convincing results and needs further improvement, but it exemplifies a ring closure strategy uncommon in coupler synthesis, which is made available by a temporarily electrophilic sulfur atom.

## 5. ORGANIC SULFUR COMPOUNDS AS INGREDIENTS IN COATING COMPOSITIONS FOR THE MANUFACTURE OF PHOTOGRAPHIC MATERIALS

### 5.1. Organic Sulfur Compounds in the Coating Process

The role of nucleophilic sulfur in manufacturing appears negligible. Contrarily, many of the ionic surfactants used to prepare solid particle dispersions or dispersions of dissolved photographic components such as couplers contain sulfonate groups. Most of the surfactants used as coating aids are also based on sulfonate or sulfate groups as the hydrophilic moiety. Among them, substituted ammonium salts of perfluorooctanesulfonic acid are especially important since this type of coating aid exceeds other types of anionic surfactants in wetting efficiency and dynamics of occupying newly created surfaces.

### 5.2. Organic Sulfur Compounds as Hardeners for Photographic Gelatin

Photographic processing today is no longer the time-consuming business it had been until 1970 and in many cases also later. In general, photographic material of any kind is processed at temperatures where native gelatin – and with it the light-sensitive components – melt away from the substrate. Current photographic materials are capable of withstanding processing temperatures above  $40^\circ\text{C}$  ( $> 100^\circ\text{F}$ ).

Permanent hardening makes gelatin layers stable almost to the boiling point of water, by stabilizing its helix structure, reducing its swelling behavior due to uptake of water or processing solution, and finally makes it surprisingly resistant to scratching even in its wet state. Permanent hardening of photographic layers is effected by crosslinking

gelatin, either by linking different polymer chains of gelatin with bridging elements provided e.g. by two or more alkylating or acylating groups present in a hardening agent, or by directly linking the most pronounced nucleophilic species in gelatin, its amino groups, directly to carboxyl groups which have undergone "activation". Since most of these reactions are proceeding very rapidly, the particular type of hardening reaction was commonly called "instant hardening".

### 5.2.1. Bis-vinyl Sulfones as Hardeners (Fig. 26)

Among other unsaturated compounds capable of undergoing conjugate additions, acryloylated compounds such as 1,3,5-trisacryloylhexahydro-s-triazine have been used as slow hardeners for many years. The analogous 1,3,5-trisvinylsulfonylhexahydro-s-triazine [75] exhibits considerably higher reactivity, but commercially interesting procedures for its synthesis via the highly toxic starting material vinylsulfonamide [76] have not been available.

Divinylsulfone has been claimed as a fast-reacting hardener for gelatine rather early [77] (1944), but its high toxicity and volatile character prevented it from being used in manufacture. Moreover, divinyl sulfone was found to be little efficient as a crosslinking agent, since its reactions with primary amino groups proceed preferably by cyclization to tetrahydrothiazine-*S,S*-dioxides. This is avoided by introducing spacer groups separating different vinylsulfone groups of a potential hardener.

Suitable *bis*- or poly-vinylsulfones useful as hardeners (**82**, **83**, **84**) for photographic layers are shown in Fig. 26 [78].

Their hardening efficiency is high, but it may take several days after drying to approximate the final state of swelling and scratch resistance. To some degree, the hardening rate of vinylsulfone derivatives can be activated by weak bases, e.g. tertiary amines or salts of weak acids.

### 5.2.2. Carboxylate Activating "Instant Hardeners": Carbamoylpyridinium salts and Sulfonylpyridinium Salts (Fig. 27)

In principle, any peptide-coupling reagent should be capable of being used as an "instant hardener" for gelatin [79]. Most of the known instant hardening systems are capable of activating the carboxylic groups of gelatin directly, by forming intermediate mixed anhydride groups or active ester groups. Many interesting instant hardeners show strong differences in reactivity and even more in crosslinking efficiency.

Among three different structures, **85** shows the highest efficiency and acceptable stability [80]. In aqueous solutions however, small concentrations of chloroformylmorpholine, a known carcinogen, are found, resulting from an equilibrium between

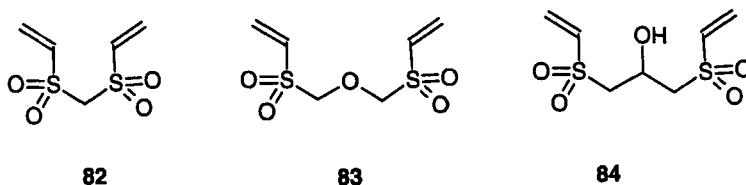


FIGURE 26 Typical vinylsulfone hardeners.

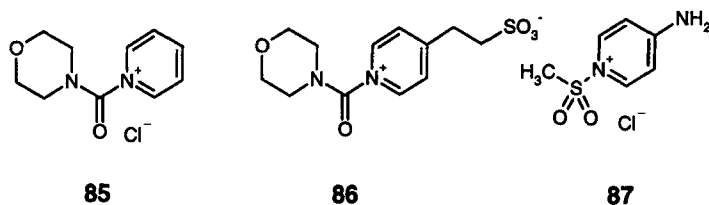


FIGURE 27 Carboxylate-activating Acyl- and Sulfonylpyridinium salts.

starting materials and product. Apart from this, there are objections against the unpleasant smell of pyridine.

Use of **86** [81] as an instant hardener helps to avoid this disadvantage because of its zwitterionic character, thus demonstrating the value of an internal counter-ion showing negligible nucleophilic reactivity. The hardener concentration needed for adjusting a comparably high degree of hardening is almost twice as high as that of **85**, measured by the degree of swelling.

It must be kept in mind that rash reaction of the instant hardener with gelatin leads to a higher degree of irregular crosslinking, where the helical structure of gelatin is not recovered even after prolonged drying and the mechanical properties of the dried layer, especially with regard to brittleness, are far from ideal.

The use of **87** as an instant hardener avoids the use of carbamoylchloride as the starting material. The compound is obtained by reacting methanesulfonyl chloride with 4-aminopyridine and is found free from 4-methanesulfonamidopyridine [82]. With regard to the swelling properties of the hardened layer, the degree of hardening is adequate, but the hardened layer shows a comparatively low resistance to scratching. This demonstrates that the degree of carboxylate activation is inferior and considerable amounts of the active sulfonylpyridinium ion must have reacted directly with amino groups instead of the carboxyl groups. Moreover, the 4-aminopyridine resulting from the transfer of the sulfonyl group to other nucleophiles is found to induce photographic fog. In contrast to 4-aminopyridine which reacts at the ring nitrogen, 2-aminopyridine is found to undergo smooth sulfonation at the amino group, and the stable sulfonylation product shows no signs of instant hardening activity.

The observed preference of the electrophilic sulfonyl group in **87** for nitrogen appears somewhat surprising, but it corresponds well to the unexpectedly low reactivity of the carbamoyl group in **86** towards amines as nucleophiles.

Among the examples of instant hardeners shown, only **86** is capable of fulfilling the requirements of an industrially used instant-hardening agent for gelatin in photographic layers. Its photographically inert character is owed to the products of its hydrolysis; morpholine-*N*-carbamate and pyridine-4-ethanesulfonic acid, and consequently also to the proper choice of the starting materials.

### 5.3. Polythiophenes as Antistatics (Fig. 28)

For many years, the photographic industry had a strong demand for permanent anti-static agents instead of electrically conducting salts such as alkali metal polyacrylates or polystyrenesulfonates.

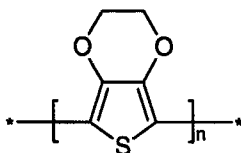
PEDT-polymer **88**

FIGURE 28 PEDT-polymer 88.

Antistatic agents are used to prevent photographic material from suffering damage by electrostatic charges which are readily generated when the photographic layer is moved along the backing layer under pressure or when it is rapidly removed from it, even under conditions of low adhesion. On photographic emulsions, tree-like or otherwise irregular discharge patterns are observed as a kind of "extra-exposure". In the course of production, a photographic material has to undergo several winding and unwinding procedures which are the primary source of potential damage.

To prevent electrostatic charges from damaging the light-sensitive layers, two different strategies can be followed:

- preventing charges from accumulating by reducing the triboelectric response,
- taking care of incurred charges by making the material electrically conducting.

Both can be done by applying antistatic agents, essentially as antistatic layers. It certainly creates more difficulties to prevent static charges from emerging, and therefore the strategy of eliminating charges has been found more promising. Older type photographic materials had been protected by layers containing low molecular and/or high molecular electrolytes, mainly as alkali salts of polymer carboxylic or sulfonic acids. Once the cations had undergone exchange by earth alkali metal ions in the course of development, the antistatic effect deteriorated.

Fortunately it was found that certain weakly colored electrically conducting polymers such as the polymerization products from 3,4-alkylenedioxythiophenes (PEDT) possess high and permanent electric conductivity once they have undergone some kind of doping as the result of the oxidative polymerization procedure.

Suitable polymers of 3,4-ethylenedioxythiophene [83] can be made in the presence of poly-styrenesulfonic acids (**88**) and coated onto the backing layer of photographic film together with gelatin. The dried layers appear bluish, show low light-scattering and high transparency, and exhibit high permanent electric conductivity.

The introduction of PEDT-protected film base marks a breakthrough in safe production for color film. Thus, photographic films carrying antistatic layers based on special "PEDT"-polymers [83b] are protected against electrostatic charging throughout all stages of production and processing. In addition, they show no subsequent attraction to dust in the finished state which has made repeated flawless printing possible.

#### 5.4. Organic Sulfur Compounds as Biocides

In the photographic industry, benzisothiazolones have replaced the common phenolic biocides to a large degree as reliable biocides preventing mold and bacterial growth

in coating solutions and coating equipment [84]. It should be kept in mind that *N*-substituted isothiazolones and especially *N*-substituted benzoisothiazolones are also valuable oxidative stabilizers, used to prevent fog in chemical sensitization [85].

## 6. SULFONE, SULFONAMIDE AND MISCELLANEOUS FUNCTIONAL GROUPS IN PHOTOGRAPHIC BUILDING BLOCKS

### 6.1. Sulfone, Sulfoxide and Sulfonamide Groups in Coupler Solvents

The highly polar character of the sulfone group and its high stability makes it an attractive tool for influencing dye formation and the properties of the dye formed, in particular its absorption. Addition of sulfones in general leads to increased absorption of water by a solvent. The same applies even more to sulfoxides. Along with sulfones, sulfoxides have been occasionally claimed as coupler solvents or cosolvents improving coupling activity and leading to higher photographic speed [86].

It is commonly believed that color couplers undergo an increase in reactivity when incorporated into a polar medium, mainly due to enhanced deprotonation. Sulfones as solvents are capable of providing a polar medium; but in spite of their high solvent power for aromatic moieties, they play only a marginal role as solvents in the chemistry of dye-forming layers. One of the reasons for this can be seen in the fact that the dipole moment of tricresyl phosphate, which has been used as the coupler solvent of choice in color photographic materials from the beginning, is comparably high.

In ordinary coupler solvents such as tricresyl phosphate magenta couplers of the pyrazolo[5,1-*c*](1,2,4)triazole class show low coupling activity, and for some years there has been considerable activity in coupler research to increase the coupling rate and dye yield of pyrazolo[5,1-*c*](1,2,4)triazoles. Activation of pyrazolo[5,1-*c*](1,2,4)triazoles by use of 3-acylamino-4-hydroxyphenylsulfones [87] or certain sulfonanilides as coupler solvents has turned out as a promising method. Occasionally however, marginal coupling activity leading to bluish discoloration is found when this type of coupler co-solvent is used in high concentrations (Fig. 29).

A sulfone group which diminishes the basicity of the aromatic amino group appears essential for the efficiency of certain *N*-4-alkoxyphenyl-thiomorpholine-*S,S*-dioxides, by which the low light-stability level of magenta azomethines from pyrazolotriazole couplers is at least doubled [88].

### 6.2. Sulfone Groups and Sulfonamide Groups in Couplers

#### 6.2.1. Pivaloylacetanilide Type Yellow Couplers

In two-equivalent yellow couplers of the pivaloylacetanilide series, 4-sulfonylphenols have been used as leaving groups for many years [89]. Other means for activating pivaloylacetanilides were ballasting anilide groups bearing sulfone or sulfonamide groups. Compound 93 bears both, a sulfone group and a sulfonamide group. In two-equivalent yellow couplers of the pivaloylacetanilide class for printing materials as an example, hue and light stability of the dye may be critical and measures for optimizing them may be incompatible with other stability demands. Simultaneously, coupling rate and dye yield depend strongly on the constitution of the leaving group.

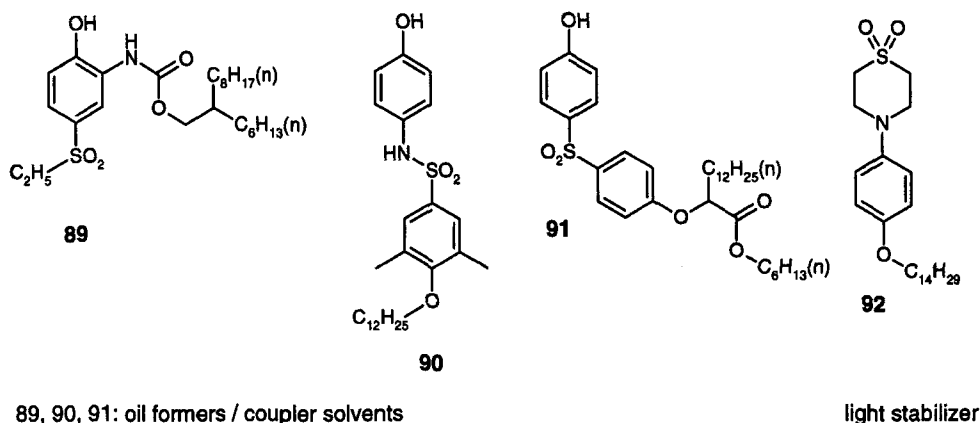


FIGURE 29 Sulfone groups in color-photographic additives.

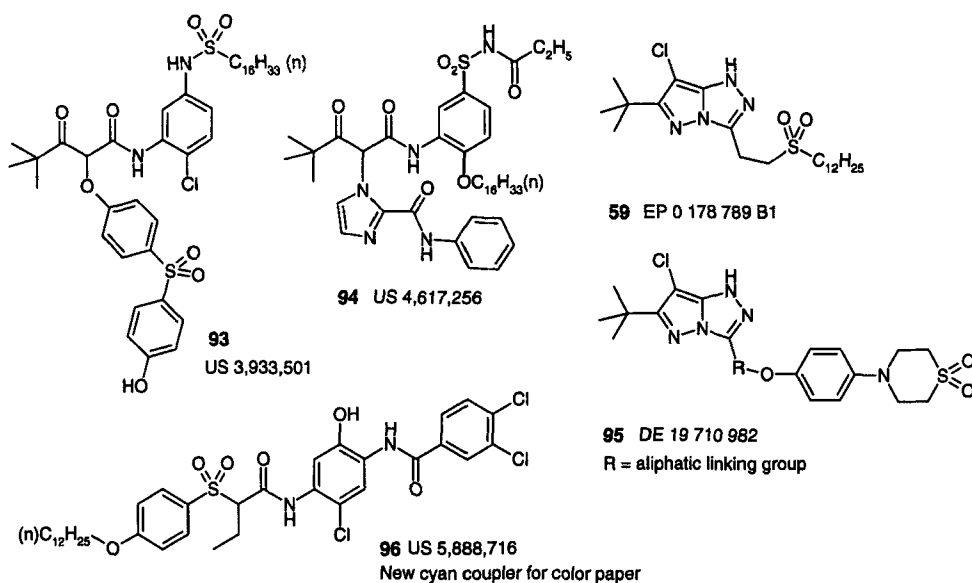


FIGURE 30 Coupler structures bearing hydrophilic sulfone and sulfonamide groups.

It has been found that pivaloylacet-(2-alkoxy)anilides bearing a sulfonamide group in the anilide part of the molecule give favorable results. High overall coupling reactivity and low dependence on alkalinity of the developer are achieved by acylation of the sulfonamide group, in combination with derivatives of imidazole-2-carboxylic acid as leaving groups. In addition, acylation of the sulfonamide group leads to an increase in solubility of the coupler [90]. An example for this is compound **94** (Fig. 30).

### 6.2.2. Pyrazolo(1,2,4)triazole Type Magenta Couplers

As in other classes of couplers, sulfone groups have been introduced into couplers of the pyrazolo[5,1-*c*](1,2,4)triazole class mainly to improve their reactivities or the absorption

of the dyes [91]. The incorporation of a moderately electron-donating 4-alkoxyphenylthiomorpholine-*S,S*-dioxide substituent into pyrazolo(1,2,4)triazole type magenta couplers of general formula **95** has been claimed as an efficient measure for improving the light stability of the chromophore [92].

In contrast to carbonamide groups, sulfonamide groups improve the solubility of a coupler in protic media in general and also its compatibility with water taken up by the coupler solvent. It is not surprising that incorporation of sulfonamide groups or sulfamide groups into couplers of the pyrazolo[5,1-*c*](1,2,4)triazole class provides an efficient measure for increasing the dye yield.

### 6.2.3. 2-Acylamino-5-(2-sulfonyl-2-alkyl)acetaminophenol cyan couplers

From 1986, Eastman Kodak has claimed novel phenolic cyan couplers of the diacylaminophenol type, where the 5-acylamino group, in later disclosures optionally the 2-acylamino group, bears an  $\alpha$ -sulfone group [93]. Cyan couplers bearing a sulfone-substituted 2-acylamino group have been claimed to show also high coupling reactivity. The dyes resulting from coupling with CD-3 and CD-4 are unusual with regard to absorption and stability level, at least in optimized structures.

As the most spectacular feature of **96** (Fig. 30), a cyan coupler for color paper introduced in 1999, the unexpectedly low  $\lambda_{\text{max}}$  of its CD-3-dye (640 nm) is noticed. The clear cyan hue is caused mainly by an exceptionally steep absorption band which keeps the green remission high. This unusual absorption profile is owed to the  $\alpha$ -sulfonylacylamino group, although in combination with an appropriately substituted 2-acylamino group. Even more surprisingly, the CD-3-dye is highly stable to dark-fading, and keeps pace with the stability level of azomethines dyes from cyan couplers of the pyrrolotriazole class. The light stability equals that of 2-acylamino-4,6-dichloro-5-ethylphenol type cyan couplers.

## 6.3. Sulfur-Containing Heterocyclic Functional Groups

### 6.3.1. Acyliminothiazolines as Functional Groups in Couplers

*N*-Cyanacetyl-benzothiazolone-2-imines **97** (Fig. 31) have been disclosed more than 60 years ago as magenta couplers, but due to low color strength they have not found industrial application [94]. Malonyl-benzothiazolone-2-imines **98** exhibit high activity as DIR-couplers and also excellent stability [95]. The hue of the azomethine dyes formed corresponds to a muddy yellow which appears less disadvantageous than the bright yellow dye obtained from DIR-couplers of the malonanilide or acylacetoanilide classes when these couplers are used in layers determined to yield a magenta or cyan dye.

### 6.3.2. Benzo(1,2,4)thiadiazine-1,1-dioxide-3-acetanilides as DIR-couplers [96]

This class of couplers, as exemplified by compound **99** (Fig. 31), has been known as yellow couplers for many years, but it has found little appreciation, because of the orange hue of the respective azomethine dyes. The acidity of these couplers is unexpectedly high, they dissolve readily in alkaline media and their coupling activity is found to exceed that of the corresponding quinazolinone-2-acetanilides (e.g. **67**).



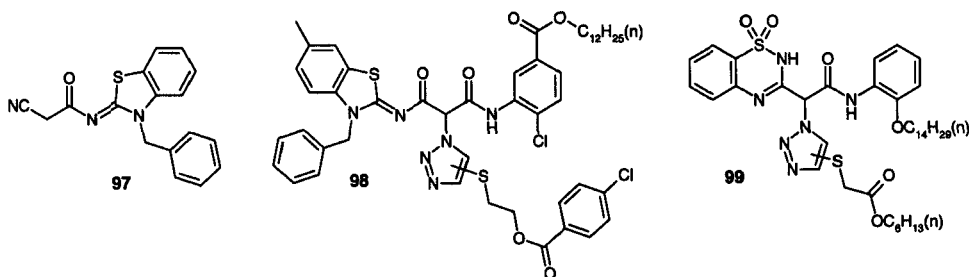


FIGURE 31 Couplers containing various heterocyclic structure elements.

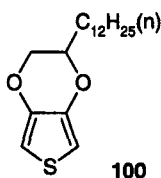
3,4-Alkylenedioxythiophene  
type light stabilizer

FIGURE 32 3,4-Alkylenedioxythiophene type light stabilizer.

As DIR-couplers, triazole-substituted benzo(1,2,4)thiadiazine-1,1-dioxide-3-acetanilides are highly efficient, and it has been demonstrated that DIR-couplers of this type are capable of inducing appreciable inhibition effects even in combination with silver chloride emulsions which usually show low response to inhibition, due to fast development. The high price of 2-aminobenzenesulfonamide as the starting material has turned out as a major obstacle impeding the technical use of these couplers.

#### 6.4. Thiophenes

3,4-Alkylenedioxythiophenes (Fig. 32) bearing a ballasting group preferably at the alkyne bridge, such as **100**, have been found capable of increasing the resistance to light-fading of azomethine dyes from pyrazolo(1,2,4)triazole magenta couplers without detrimental effects [97]. The daylight-fading rates are diminished by about 50%, depending on the initial density. In analogy to the supersensitizing efficiency of alkylenedioxythiophenes, it is assumed that single electron transfer from the electron-rich thiophene to the excited singlet state of the dye is responsible for the rapid deactivation of the excited dye.

#### 6.5. Redox-dye-releasing Compounds: The Sulfilimine Dye-releasing System [98]

As an exception to self-imposed limits, and simultaneously as a contribution of color diffusion to sulfur chemistry, a reductively cleaved dye-releasing system has to be mentioned, where the usual functions of silver halide and dye-releasing chemistry have been arranged in an, at first sight, unexpected and not easily understood way.

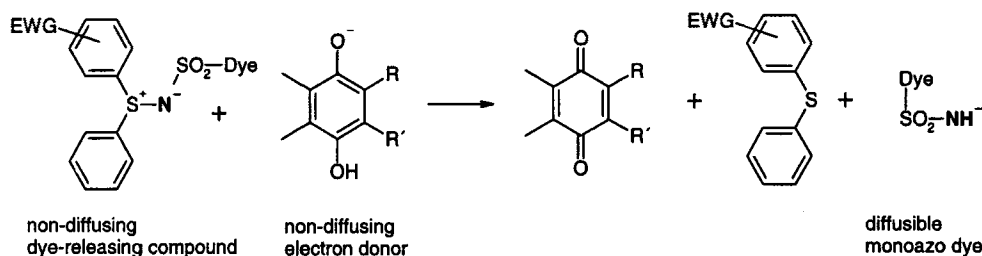


FIGURE 33 Reductive cleavage of a sulfilimine-type dye-releasing compound.

Color diffusion chemistry has played an important role between 1970 and 1985 [99] when instant imaging systems were highly desired. To understand the principles of the color diffusion system, one has to take into consideration that color diffusion systems are based on preformed dyes which are transferred to an image-receiving system after imagewise discrimination, where dye is

- either mobilized (Fuji Fotorama instant photographic system)
- or immobilized (Polaroid Polacolor and Image system).

Most preferably but not exclusively, dye is mobilized by a redox reaction, either by oxidation and or by reduction.

The preferred mode of dye mobilization is splitting of a dye from a non-diffusing carrier. The preferred functional splitting groups are:

- sulfinate groups [100],
- sulfonamide groups [101].

Instant-imaging color diffusion systems are operating by the direct-positive mode; i.e. exposure to light leads to the absence of dye in the picture. If this has to be achieved by use of normal negative-type emulsions, where exposure and subsequent photographic development generates "oxidation equivalents", oxidation equivalents are used to prevent the dye from diffusing to the image-receiving unit.

A preferred mode consists in competition between silver halide, as one oxidant, and a dye-providing compound, as the other oxidant, for an additional, preferably non-diffusing, electron donor. Development of silver halide in the presence of an electron-transfer agent leads to exploitation of the electron donor which consequently loses its capability of releasing diffusible image dye.

In the sulfilimine "CR" system [98] (Fig. 33), an image dye, preferably of the monoazo type, is bound to its non-diffusible carrier by an *N*-sulfonyl-*S,S*-diarylsulfilimine group which is sufficiently stable to hydrolytic attack by alkaline media, but readily releases a dye-sulfonamide, when it is reduced by an electron donor of the substituted hydroquinone type (*Cleavage by Reduction*).

## 7. FINAL REMARKS

Sulfur compounds are indispensable components of all photographic systems based on silver halide emulsions. Sulfur compounds of the low valence states, mainly of

oxidation number  $-2$ , such as thiols, thioethers, thioamides or heterocyclic thiones strongly coordinate to silver ions, either in solution or on the surface of silver halide microcrystals, forming soluble or insoluble silver complexes, and thus influence the photographic process.

Besides the coordination behaviour of low valent sulfur compounds, the participation of thiols or tautomerizable thiones in the reduced state, and disulfides, thiol sulfonates or sulfenamides, as examples of sulfur compounds bearing a sulfur-heteroatom bond, in the oxidized state of sulfur-based photographic redox systems exemplifies another role of sulfur as a "modifier" in all stages and modifications of photographic processing.

Compared to the lower valence states, sulfur compounds of the positive oxidation numbers, especially  $+2$  and  $+4$ , are of minor importance for the silver halide part of photographic systems. In color photographic materials however, they play particular roles in the chromogenic part of the system.

Generations of chemists engaged in the advancement of silver halide photography have had the experience that sulfur compounds provide unique and indispensable tools for optimizing light-sensitive silver halide emulsions, chemical building blocks, processes, production safety and more. Most of these tools have never raised the attention of sulfur chemists, and almost nothing has challenged their state of knowledge. Not only from the viewpoint of chemistry, but also of photography, most of the solutions were temporary in nature, with the clear intention of reoptimizing any system on demand, either under economical constraints or under the aspect of technical evolution.

Most of the chemistry presented in this article has been gathered from patents, where the interests of intellectual property and protection of technical know-how have clearly overruled more strictly scientific questioning. True advantages of inventions may often remain unnoticed.

Sulfur as the "Swiss knife of photographic chemistry" – why not? Beside silver and the halogens, the role of sulfur in photography, in particular of organic sulfur compounds containing nucleophilic sulfur atoms, might exceed that of any other element except nitrogen.

Within about twenty years, the present photographic knowledge may be historical: its targets, its compromises and its triumphs, but also its high quality criteria. There are good reasons for documenting as much of its chemical highlights as possible – now.

For more than 31 years, the author has been engaged in chemical research for photographic products. He has had the opportunity of contributing to solutions for quite a number of problems encountered, and to look into details. Most of the work done was determined to support classic consumer products in color photography, such as color negative film, color reversal film and color paper.

Photographic color diffusion systems, a well-known example for temporary challenge and transient solutions, have never reached the importance of the film-and-paper market. Since the concepts of color diffusion chemistry have been given up almost totally, there is no demand for discussing them in spite of their high degree of sophistication, and, with one exception of theoretical interest, they have remained outside the scope of this review.

It is to be expected that semiconductor technology and digital photography will take most of the place of silver halide photography, and there will hardly be a place for sulfur in photography any more.

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