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SX-70: A UNIQUE SYSTEM OF DYES

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SUMMARY

The unique dye system incorporated in the Polaroid SX-70 photographic system is described and the mode of operation of the film in use is explained.

1. INTRODUCTION

While the SX-70 photographic system is based upon conventional silver halide photography, its success depends on the complex interactions of a system of dyes unique in photographic science and technology. The system incorporates the application of cyanine sensitizing dyes, of image-forming dye developers derived from numerous classes of dyes, and of specially designed opacification dyes based on indicator dyes of the phthalein class.

The purpose of this article is to show how these diverse dye types are combined to produce beautiful photographs in colour by the simple operation of aiming a camera and then pressing a button. The dry, blank incipient photograph is handed to the photographer who then can literally watch it form the colour image before his eyes.

2. OPTICAL SENSITIZATION

The first dyes to act in the chain of events are the sensitizing dyes. These are required to extend the inherent sensitivity to light of silver halides from the blue region to the green and red regions. The theory of optical sensitization is covered in many articles and books. James[1] discusses it at length, and the photographic literature abounds in articles devoted to the discussion of how a sensitizing dye adsorbed on the surface of

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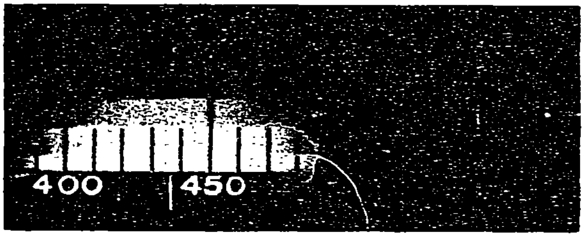

Fig. 1. The inherent sensitivity of a silver halide emulsion to light. The wavelength scales in Figs. 1–3 are in nanometres.

silver halide crystals transforms a quantum of absorbed light into a silver atom. The action of sensitizing dyes is shown in Figs. 1–3. Figure 1 is the wedge spectrogram showing the spectral distribution of the sensitivity of a silver halide emulsion to light. This sensitivity is called 'inherent', and it extends only into the middle blue region. The sensitivity in the ultraviolet is largely unused in most photographic systems. In SX-70 photography the ultraviolet is filtered out by u.v. absorbing dyes in the cover sheet and by the camera lens.

Thus, to extend the sensitivity to the green (Fig. 2) and the red (Fig. 3) regions appropriate dyes are added to the silver halide emulsions before they are coated on the film base. Typical dyes are also shown in Figs. 2 (green) and 3 (red).

At this point the photographer has aimed his camera at the subject to be photographed, and has pressed the button to take the picture. The act of pressing the button sets a complex series of events in the camera into motion. The sonar rangefinder focuses the lens, the viewing mirror flips up to reveal the film surface, the shutter opens and actuates the automatic exposure control system, the shutter

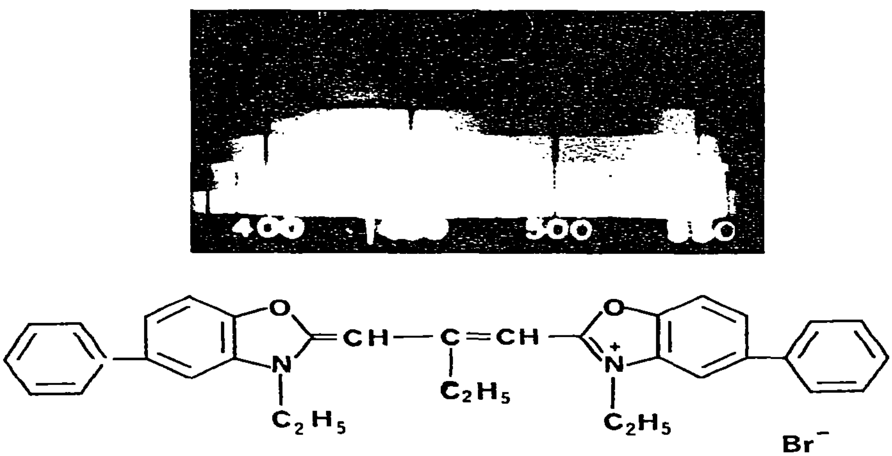

Fig. 2. The sensitivity of the emulsion of Fig. 1 optically sensitized with the green sensitizing dye shown.

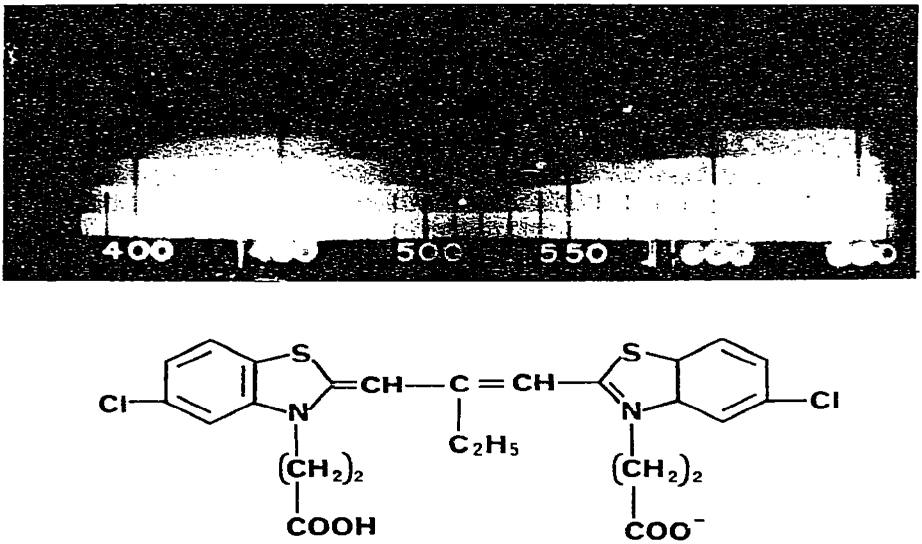

Fig. 3. The sensitivity of the emulsion of Fig. 1 optically sensitized with the red sensitizing dye shown.

closes to actuate the motor that drives the exposed sheet of film through the rollers which break the pod to spread the processing reagents uniformly over the surface of the film. The exposed and now processing film is ejected from the camera.

3. IMAGE FORMATION

The breaking of the pod now initiates a series of chemical events which must occur at the right times similarly to the complex series of mechanical events that occurred in the camera.

The image-forming material is the dye developer. A detailed description of the synthesis and properties of dye developers has been given by Bloom *et al.*[2] and by Land *et al.*[3] References 2 and 3 also show schematically the construction of an SX-70 film unit both before exposure and during processing.

Basically, the dye developer concept[4] (Fig. 4) consists of joining a coloured moiety (dye) to a photographic developer moiety (developer). When exposed silver halide is reduced to metallic silver, the oxidized dye developer becomes immobilized. The unoxidized dye developer remains in solution in the alkaline pod reagent. It diffuses from the negative through the pod reagent to the image-receiving layer where it is bound by mordants in the receiving sheet. More complete descriptions of the diffusion transfer process may be found in references 2 and 3.

In principle any dye chromophore may be used for the dye portion of the dye

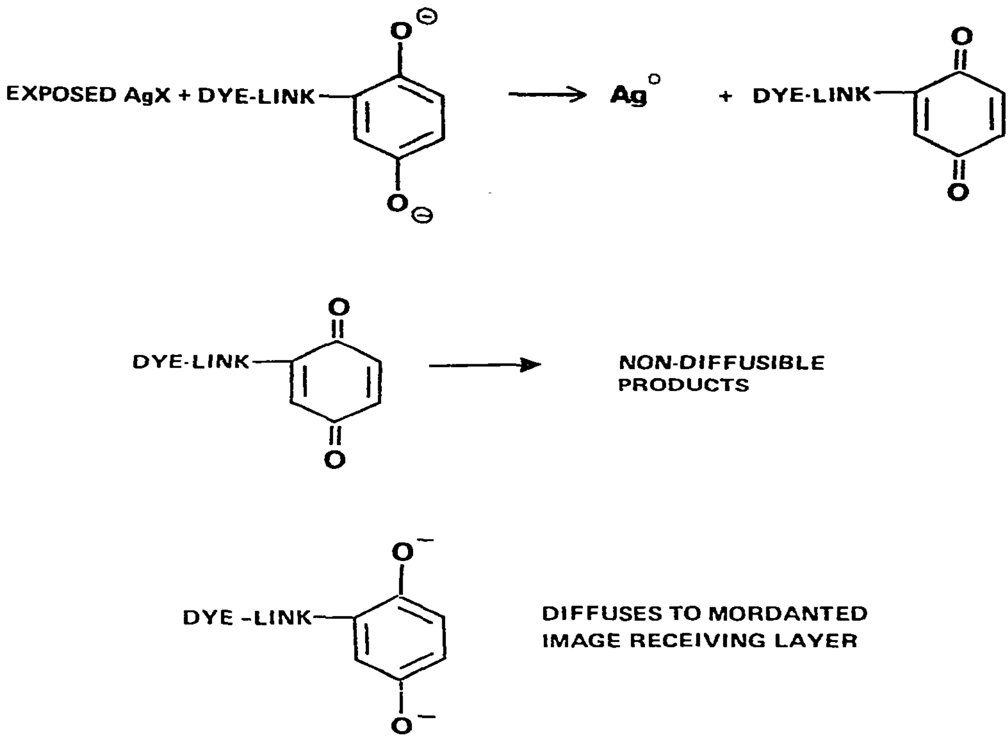

Fig. 4. A schematic representation illustrating how a dye developer is controlled by a silver halide emulsion in exposed and unexposed regions.

developer. In practice there are properties of the dye developer which restrict the selection. Some requirements for a good chromophore are the following:

The spectra of the dyes should be consistent with the requirements of three-colour subtractive colour synthesis.

The dye must be chemically stable, especially to the highly alkaline pod reagent and to the reducing nature of the developer moiety.

The spectra of the dyes should not be subject to changes in pH, as the system starts out very strongly alkaline and ends slightly acidic.

The chromophores must be photographically inert.

The dyes should be as stable toward light as is feasible with the other requirements.

Other parameters such as solubility and diffusibility must be adjusted by the synthetic chemists to provide a self-consistent group of dyes for the photographic scientists to wed into a properly functioning system.

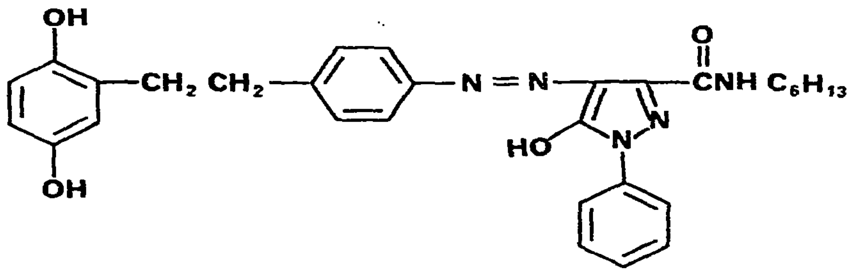

Fig. 5. Polacolor 1 yellow.

While this is a formidable list of requirements, a substantial number of dye classes is available for candidates as dye developers. Some of the many dye classes that have been successfully made into useful dye developers are the azo, anthraquinone, metal complex, phthalocyanine, quinophthalone, and xanthene dyes.[2] Fortunately, there is no restriction against the use of more than one type of dye in a set of three dyes. The dyes used in Polacolor 1, the original photographic instant colour film, and in SX-70, the original integral instant film, are presented in Figs. 5–10.

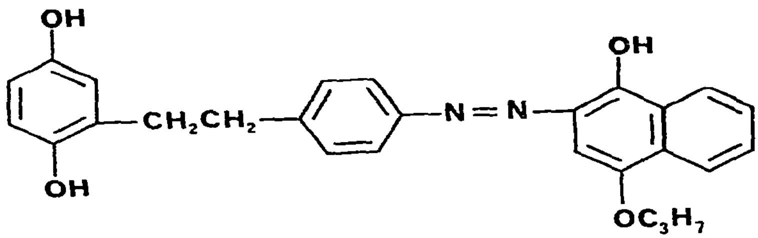

Fig. 6. Polacolor 1 magenta.

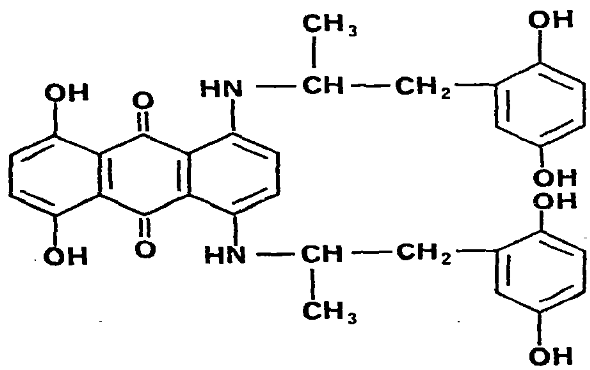

Fig. 7. Polacolor 1 cyan.

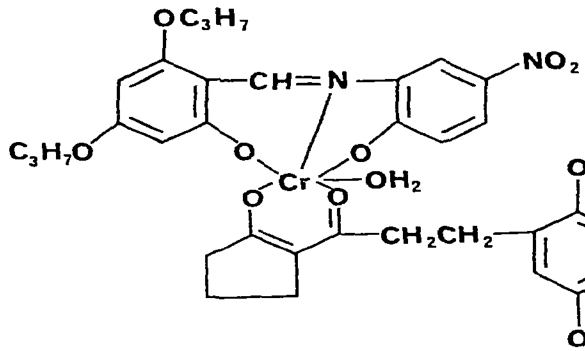

Fig. 8. SX-70. Polacolor 2 yellow.

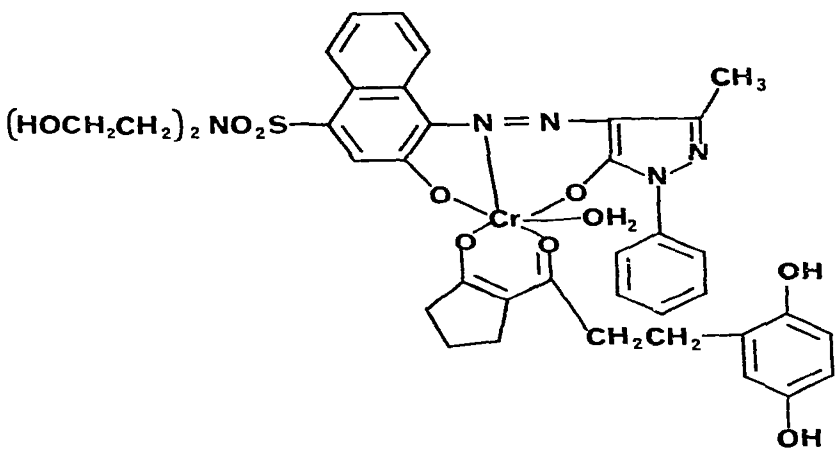

Fig. 9. SX-70. Polacolor 2 magenta.

4. OPACIFICATION: THE CHEMICAL DARKROOM

Returning now to the incipient photograph ejected by the camera, it should be noted that the silver halide is still sensitive to light, and must be shielded from the most intense light anticipated in actual use. Some of the brightest natural scenes are at the seashore on a sunny day and in sunny snow scenes. To protect the film from exposure during the processing step it was necessary to devise dyes that would absorb the light during the critical seconds after ejection from the camera.

An 'opacification dye' is a material in the reagent which protects the film from exposure to light during processing, and which disappears permanently to an

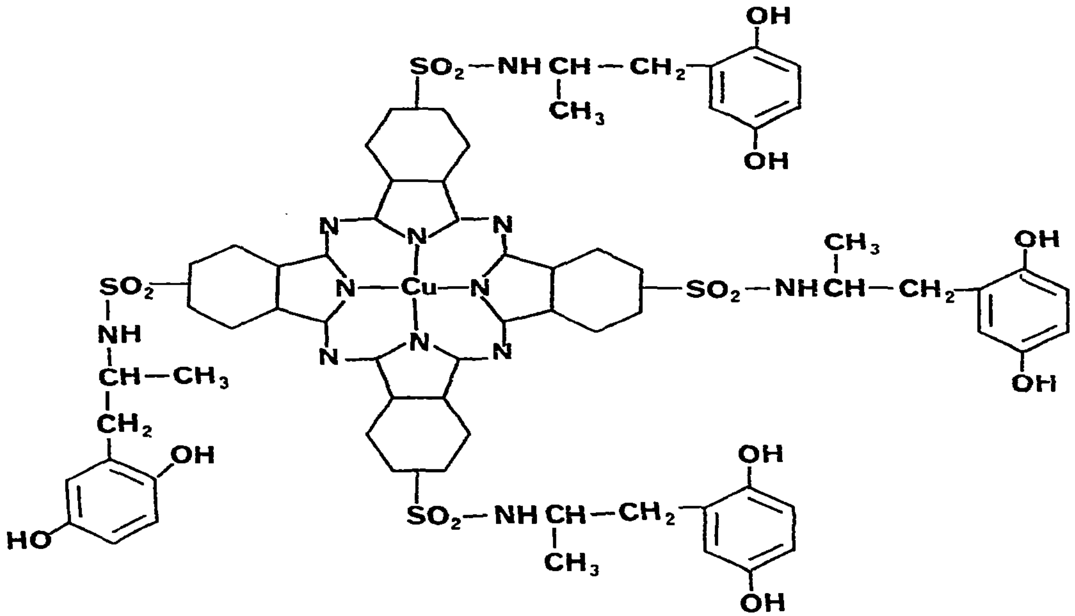

Fig. 10. SX-70, Polacolor 2 cyan.

invisible substance.[5] Just as there are requirements for good dye developers, there are also requirements for good opacification dyes. Some of these requirements are the following:

They should be stable in caustic solution for at least a year.
Since the method used to bleach the dyes is pH reduction, they must change from the coloured forms to colourless forms by lowering the pH. To ensure that they disappear early in the chemical series of events the pK_a of the opacifiers should be high.
The entire silver halide sensitive region must be protected from light during the processing step.
They must be photographically inert.

To provide materials meeting these objectives required much labour to synthesize them as well as a deep insight into the chemistry of the dyes chosen.

Of the numerous types of indicator dyes, the phthaleins provide the necessary colourless–low pH form. However, the phthaleins suffer from several deficiencies as they were known at the beginning of the research effort. They react with alkali as shown in Fig. 11. Thus, at the moderate pH 9, they become coloured and exhibit a narrow absorption band. When the pH is raised they react with hydroxide ion to form a new, colourless form. When in contact with substantial excess of base for a

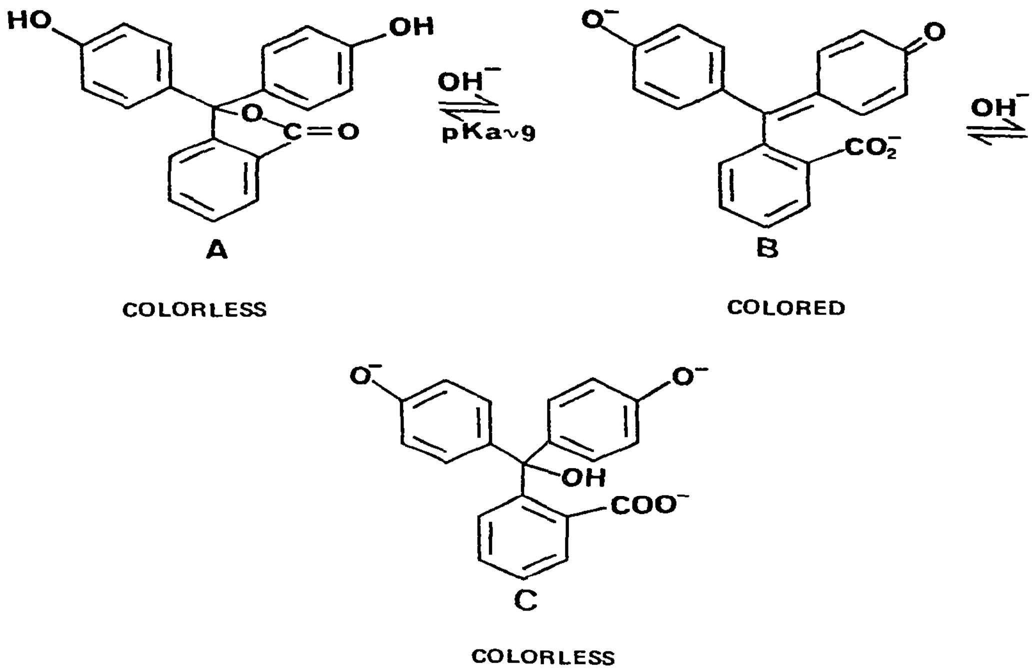

Fig. 11. The reactions of phenolphthalein with hydroxide ion. These reactions are reversible with acid, but the colourless, hydroxylated form, C, slowly decomposes in strongly alkaline solutions.

period of time, they decompose to other substances. It was necessary, therefore, to raise the pK_a, broaden the absorption spectrum, prevent them from adding hydroxide ion, and make them stable to base.

Various techniques were found to prevent the hydroxylation reaction, notably by providing steric hindrance to the access of the hydroxide ion. Introduction of the naphthalein residue (Fig. 12) was found to make the dyes stable to hydroxylation and to decomposition in strong base. An additional benefit of this device is the

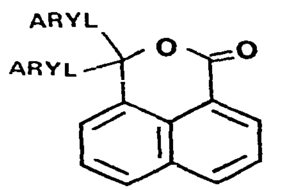

Fig. 12. Naphthaleins provide steric hindrance to the hydroxylation reaction, and the six-membered lactone raises the pK_a by about one unit when compared with the corresponding phthalein dye.

pKa₁	3.00	pKa	9.99
pKa₂	13.44		

Fig. 13. Hydrogen bonding in the salicylate anion raises the pK_a of the phenolic hydroxyl group by more than 2 units.

increase of pK_a by about one unit, caused by the larger lactone ring (6 atoms) vs the five-membered ring in the phthaleins.

Further increase of the pK_a is provided by hydrogen bonding of the phenolic hydroxyl group.[6] This is exemplified by comparing the pK_a of phenol with that of salicylic acid (Fig. 13). Note that the pK_a of phenol (9·99) is raised to pK_a 13·44 in salicylic acid by the hydrogen bonding of the phenolic group to the carboxylate anion. Other combinations of proton-donor–acceptor systems are pyrrole NH to carboxylate, phenol to ring nitrogen, and pyrrole NH to sulphonamide anion.

The absorption spectra of the phthaleins was altered by using naphthalene and indole nuclei instead of simple phenols. Long hydrocarbon chains on the opacifiers make them relatively immobile and help them to remain in the reagent layer of the system while the more mobile dye developers were able to diffuse through this layer to the image receiving layer, where they are viewed against the white TiO_2 pigment in the processing reagent.

The structures of two opacifying dyes that, combined, were selected to protect the ejected film from further exposure to light are shown in Figs. 14 and 15.

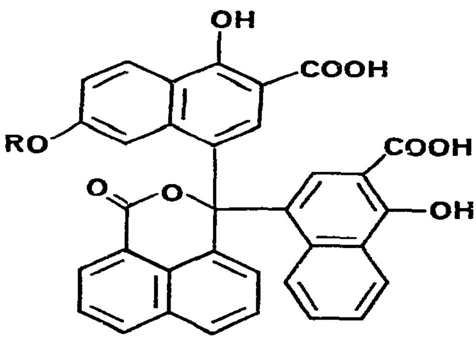

Fig. 14. Naphtholnaphthaleins have long and broad absorption spectra in alkali.

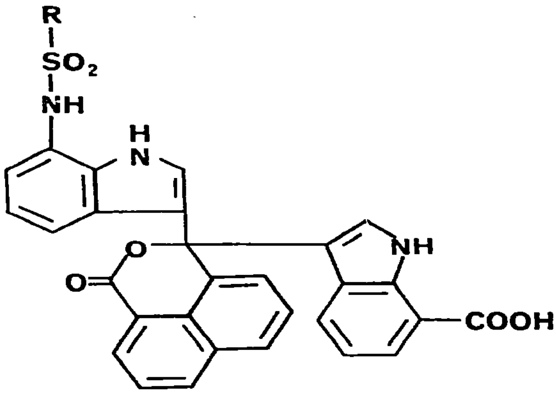

Fig. 15. Indolenaphthaleins possess short absorption bands to enable the entire spectrum to be covered.

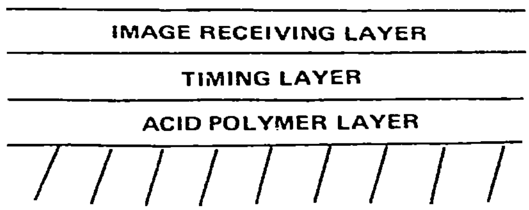

Fig. 16. A diagrammatic representation of the positive image-receiving sheet.

5. CHEMICAL SHUTDOWN: pH LOWERING

The method for lowering the pH of the SX-70 system will now be described. The receiving sheet is constructed as shown in Fig. 16. On a transparent base containing a u.v. absorbing dye is coated an acidic polymer, followed by a 'timing' layer, and then a mordant layer. The function of the 'timing' layer is to prevent the hydroxide ion from access to the acid polymer layer until the dye image has largely formed. Since this time varies with the temperature, the timing layer is designed to change with temperature to regulate the consumption of alkali. When the alkali is consumed by the acid polymer layer, the pH is lowered to a slightly acidic value, and the SX-70 system of dyes has created a full colour photograph. In the new Time Zero film the timing and acid polymer layers are coated beneath the negative layers.

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