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[54] **DIAZO PROCESS OF FORMING INFRARED ABSORBING RECORD**
20 Claims, 1 Drawing Fig.

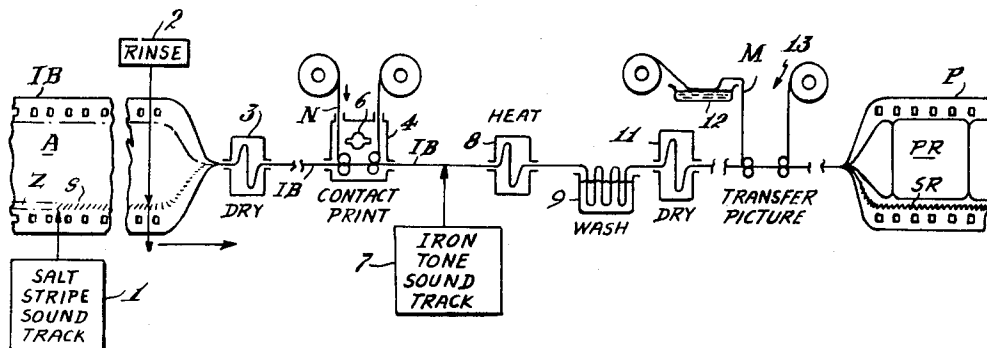
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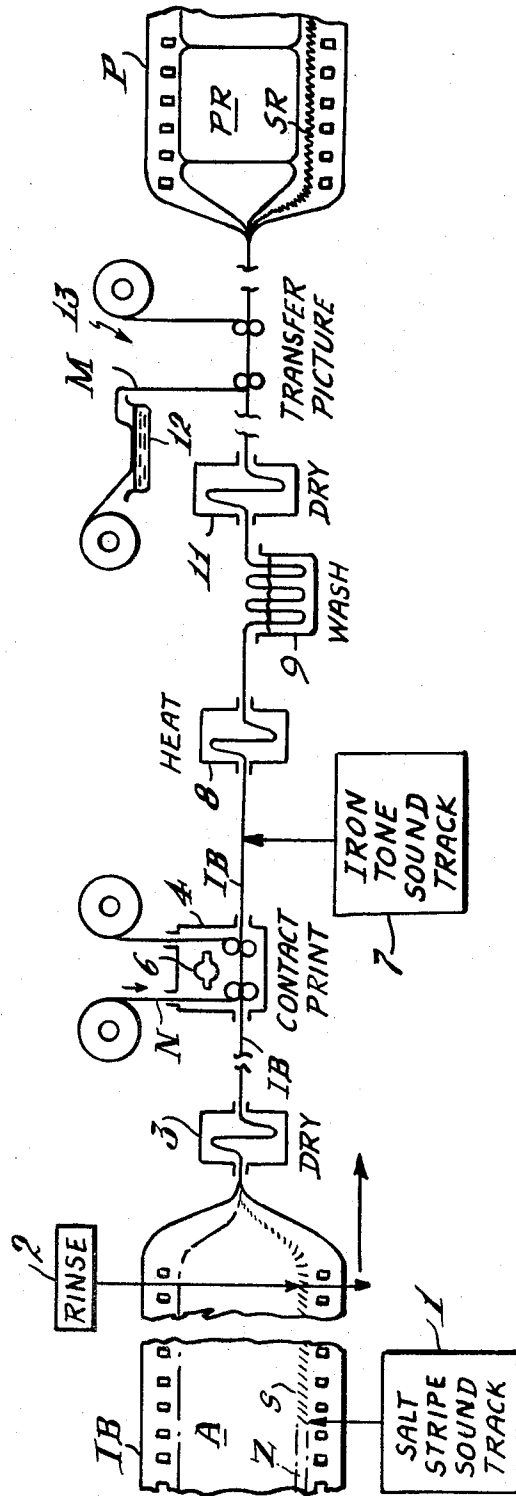
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ABSTRACT: A nonsilver soundtrack is formed on a transparent blank motion picture imbibition film by striping the longitudinal soundtrack zone only with a photosensitive diazosalt. The sensitized track is then printed from a silver soundtrack to form a latent image. The soundtrack zone only is then developed with an iron blue forming toner to produce an iron blue soundtrack record which is absorptive of infrared light universally used to excite the photocell of commercial motion picture projectors. The three-color aspects of a color motion picture are then transferred by imbibition to the picture area beside the soundtrack.





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DIAZO PROCESS OF FORMING INFRARED ABSORBING RECORD

With the increasing cost and scarcity of silver, and the prospect of its use being restricted to essential purposes, there is a pressing need for a silver substitute in motion picture production. The picture area has long been printed by a non-silver dye transfer process in which three, color dyes are successively transferred by imbibition from gelatin relief matrices to the blank hardened and mordanted gelatin of the print stock. But the imbibition dyes now used absorb very little of the infrared light to which the sound-reproducing photocells of substantially all motion picture projectors throughout the world are equipped. Consequently, it is a practical necessity to print soundtracks with a nonsilver, infrared-absorbing substance.

British Pat. No. 855,438 of Technicolor Corporation, published Nov. 30, 1960, which is incorporated herein by reference, describes a method of producing such a nonsilver, infrared-absorbing soundtrack. A soundtrack is prepared in the form of a gelatin relief record on an imbibition matrix film strip. The gelatin relief is dyed with a strong reducing action dye and the dye transferred to the soundtrack zone of an imbibition blank. The blank is then treated with ferric ferricyanide to form prussian blue (one of the several names for iron blue). Iron blue is a wholly acceptable silver substitute, having high absorption in the 700 to 1,000 nanometer infrared region, the region of maximum response of motion picture projector photocells.

Despite the satisfactory absorption characteristics of its iron blue soundtrack the above process involves the use of a special imbibition matrix, and lengthy and careful tanning, developing, and etching treatment to form the relief record. The dye in the relief matrix must be transferred to the imbibition blank in bulky apparatus along a very long, e.g., 200-foot dye transfer path. Image quality and fine detail essential to a soundtrack suffer in the etching of the gelatin relief and transfer by imbibition. Further the relief record deteriorates with each transfer thus severely limiting the number of prints which can be made.

Thus the object of the present invention is to produce an iron blue record from a less expensive raw stock and with a simpler, faster and more economical process and apparatus, which nevertheless produces a greater number of prints of higher image quality and finer detail.

According to the invention a process of producing a non-silver photographic record comprises applying a photosensitive diazocompound to a support, exposing the compound to a light image to form a latent record therein of the image, and toning the latent record with a solution of iron blue former to produce an iron blue, infrared absorbing record.

For the purpose of illustration a typical embodiment of the invention is shown in the accompanying FIGURE which shows, schematically, apparatus for printing a soundtrack record on motion picture film.

Shown at the left of the FIGURE is a conventional motion picture imbibition blank film IB comprising a support strip of cellulose nitrate, cellulose acetate-butyrate, cellulose triacetate, polycarbonate, polystyrene, polyester or similar flexible motion picture base which is coated with a layer of gelatin, polyvinyl alcohol, hydroxyethyl cellulose or like colloid. Eastman Kodak Emulsion 30-9362-1 is suitable. The colloid is hardened sufficiently to withstand wet processing and contains a mordant not incompatible with the photosensitive salt and iron toner to be described. The mordant may be a hydrous oxide of aluminum, chromium, tin or thorium, but preferably is a relatively nondiffusing cationic, high molecular weight organic material such as a synthetic polymer carrying tertiary or quarternary nitrogen groups, all of which are well known in the art.

The imbibition blank IB comprises an area A reserved for picture records and a longitudinal zone Z in which the soundtrack is produced. First a known applicator 1 stripes the soundtrack zone Z with a weakly acid, aqueous solution of a

photosensitive diazosalt such as p-diazodiphenylamine sulfate as will be described more fully. A suitable applicator is shown in British Pat. No. 660,742. The film may run at 150 feet per minute as the solution is allowed to soak into the colloid for approximately 15 seconds. It is then rapidly and briefly rinsed off away from the picture area as by a nozzle device 2 which preferably is directed as shown to wash excess solution away from the picture area A. The rinse should be brief to avoid removing the diazosalt. With fast diazosalts which tend to self-couple in a plain water rinse, the rinse is acidified with a volatile acid such as acetic acid. The blank is then immediately dried in a dry box 3. Thereafter it may be used immediately or stored for long periods.

A conventional variable area soundtrack negative N is prepared in any suitable way and with standard equipment on a normal soundtrack negative film, e.g., Eastman Kodak Emulsion 5362, black and white silver negative having a maximum density of about 1.00 and a minimum of 0.08 is suitable. To minimize image growth it is desirable to produce a density somewhat lower than the conventional optimum.

The sensitized imbibition blank IB is fed into emulsion-to-emulsion contact with the silver soundtrack negative N in a known belt printer 4. A speed of 350 feet per minute may be used with a high-pressure xenon or mercury vapor exposing lamp 6, e.g., Osram HBD-200-W2. Such lamps are preferred for their high blue and near ultraviolet emission in the 330 to 430 nanometer region of diazosalt sensitivity. A latent record of the soundtrack is thus produced in the sensitized zone in the form of a photodecomposition product of the sensitizing salt.

As in the previously mentioned British Pat. No. 855,438 the latent dye record is then toned with an iron blue former, e.g., ferric ferricyanide, applied in the soundtrack area only by a device 7 like the previously described applicator 1. The latent record is thus developed as a nonsilver, infrared-absorbing iron blue record of the original variable area soundtrack on the silver negative N. The film is then fed for 60 seconds through a cabinet 8 heated to 130° F. dry bulb and 120° wet bulb, and passed through a clean water wash 9 for 30 seconds and dried in a dry box 11 in preparation for imbibition printing of the picture area A.

By standard methods the gelatin reliefs of a series of imbibition matrices M, of which one is shown, are coated with an appropriate colored dye 12 and their graphic information is transferred by imbibition to the picture area. The final print P thus comprises the printed picture record PR and the iron blue soundtrack record SR.

In comparison with the method of British Pat. No. 855,438, the present process employs a silver soundtrack negative made by a conventional, simple and reliable process rather than by use of a special imbibition matrix raw stock, tanning development and etching. The fine-grain silver negative is appreciably less expensive than matrix stock, has much higher speed, and thus can be used on standard high-speed equipment as compared to the specialized, low-speed imbibition printer. Moreover a contact printer is much smaller and less expensive than an imbibition machine, and several times as many contact prints may be made from a silver negative as from an imbibition matrix. Finally there is a marked increase in the image quality and fine detail essential to high-fidelity reproduction of sound.

The present process may also be compared favorably with a well-known blueprint soundtrack process which employed a film sensitized with a mixture of ferricyanide and ferric oxalates or citrates. Because the film stock was sensitized prior to exposure, the iron salts might undergo a dark reaction during storage and become fogged within a few weeks, which period was shortened by the addition of mordants. Adding acid to increase sensitivity increased fogging. The sensitized blank of the present process has a shelf life of many months without fogging even with acidified salts, and its mordants are in contact with iron salts only during the seconds of processing through the iron toner 7 and heater 8 prior to the wash 8. Approximately five times greater light intensity or exposure time

was required to expose blueprint sensitized film, and yet the resulting soundtrack was barely acceptable as to contrast and density. The present process produces a soundtrack of high contrast and density and substantially greater stability under projection lighting.

A preferred sensitizing solution comprises 1 liter of water, 12 grams 4-diazodiphenylamine sulfate, and, to increase viscosity, 5 grams of commercial grade hydroxyethyl cellulose such as that sold by Hercules Powder Company under the trade name Natrosol 250 M. Other thickeners may be used, for example, hydroxypropyl cellulose sold by I. C. I. as Klucel G and Klucel M. At a pH of 1.7 the solution has a clear orange-yellow color, and is stored and applied at normal ambient temperature. Other photosensitive acid water soluble diazosalts are suitable which photodecompose to form the strong reducing agents with affinity for gelatin as are listed in British Pat. No. 855,438. The best sensitizers are derivatives of 4-aminodiphenylamine and of 4-amino-N,N-dialkyl-aniline. Commercially, high-speed diazosalts are available from General Dyestuff as Variamine Blue Salts RT FGN and BD, from Hostachem as Diazo M, from Fairmount as Sensitizer DP and Sensitizer HD-23, and from American Aniline as Fast Blue Salt VB. Of moderate speed are Fairmount Sensitizers D-16 and D-17 preferably developed with iron toner for 60 seconds at 45° and 40° C. respectively. Producing weaker but usable iron blue records are Fairmount Sensitizers DE-40, BO-1, HD-30, HD-60, HD-EB-1, DM, HD-61, HD-75, HD-85, and General Dyestuff Fast Blue Green Salt B, Fast Blue Salt BBN. Salts usable if the rinse 2 following the strip 1 is slightly acidified with acetic acid to avoid self-coupling are Fairmount Sensitizers HD-60, HD-65, and General Dyestuff Fast Black Salt B and Fast Blue Salt BN.

The iron blue toner is made of three stock preparations: the first consisting of 5 grams of Natrosol 250 M in 1 liter of water; the second consisting of 90 milliliters of water, 0.2 grams potassium dichromate to control fogging, 8 milliliters of 85 percent phosphoric acid and 16.3 grams potassium ferricyanide; and the third consisting of 200 milliliters water, 125 grams ferric nitrate-9H₂O, 40 milliliters 70 percent nitric acid and 3 milliliters of commercial polyoxyethylated fatty alcohol used to insure wetting and spreading, and sold as a nonionic surfactant by Antara Chemicals Division of General Aniline and Film Corporation under the trade name Diazopon AN. Ferric chloride hexahydrate or commercial ferric chloride solution may be substituted for ferric nitrate nonahydrate, although the latter is presently preferred. Shortly before application the iron blue toning solution is prepared by mixing 350, 100 and 85 milliliters of the three stock preparations.

While one desirable embodiment of the invention has herein been disclosed by way of example, it is to be understood that the invention is broadly inclusive of any and all equivalents which fall within the scope of the appended claims.

I claim:

1. The process of forming a nonsilver photographic record on a photographic support which comprises:
applying a photosensitive diazocompound to the support,

said diazocompound forming a reducing agent by photodecomposition,

exposing the compound to light imagewise to form a latent record therein of the image in the form of a reducing agent in the exposed areas, and

toning the latent record with a solution of iron blue former which comprises a water soluble ferric salt, a water soluble ferricyanide compound and an acid, to produce an iron blue infrared absorbing record in the exposed areas.

2. The process according to claim 1 wherein the light image is formed by exposure through a silver image in a photographic emulsion.

3. The process according to claim 2 wherein the support comprises a sensitized emulsion brought into emulsion-to-emulsion contact with said silver image emulsion.

4. The process according to claim 1 wherein the soundtrack zone only of a motion picture film is striped with diazosalt.

5. The process according to claim 4 wherein the soundtrack zone is rapidly rinsed and dried after striping.

6. The process according to claim 4 wherein the striped soundtrack zone is brought into contact with a photographic soundtrack record during exposure.

7. The process according to claim 6 wherein the soundtrack is a negative silver record on a motion picture film.

8. The process according to claim 7 wherein the striped soundtrack zone is brought into emulsion-to-emulsion contact with the silver soundtrack record.

9. The process according to claim 1 wherein the exposure is with a lamp having high emission of ultraviolet and blue light.

10. The process according to claim 4 wherein the exposure is with a lamp having high emission of ultraviolet and blue light.

11. The process according to claim 4 wherein the soundtrack zone only is toned with iron blue former.

12. The process according to claim 1 wherein the toned latent record is then washed and dried.

13. The process according to claim 11 wherein the toned latent record is then washed and dried.

14. The process according to claim 12 wherein the wash is neutral to acid.

15. The process according to claim 13 wherein the wash is neutral to acid.

16. The process according to claim 4 wherein the area of the motion picture film adjacent the soundtrack zone is then printed with graphic information by imbibition from a gelatin relief matrix.

17. The process according to claim 1 wherein the diazosalt is selected from the group consisting of a 4-diazodiphenylamine salt and a 4-diazo-N,N-dialkyl-aniline salt.

18. The process according to claim 4 wherein the diazosalt is selected from the group consisting of the salts of paraphenylenediamine, para-aminodiphenylamine and 4-diazodiphenylamine.

19. The process according to claim 1 wherein the diazosalt is 4-diazodiphenylamine sulfate.

20. The process according to claim 4 wherein the diazosalt is 4-diazodiphenylamine sulfate.

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