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**PHOTOGRAPHIC HYDROXYETHYL STARCH
SILVER HALIDE PRINT-OUT COMPOSITION**

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The present invention relates broadly to photosensitive compositions and more particularly to photographic compositions of the "print-out" type. The term "print-out" refers to that type of photosensitive substance upon which a visible image is obtained after an exposure to light or other electromagnetic radiation has been initially utilized to form a latent image, the visible image being obtained initially or simply by an additional exposure to such radiation, normally at a somewhat lower intensity. This additional exposure is known as "latensification" and is general in its application, including exposing the area upon which the initial image was formed as well as the surrounding background area to an added amount of radiation. Print-out emulsions or dispersions are distinguished from development emulsions which require a development treatment such as a chemical development after initial exposure to produce a visible image, inasmuch as this image is produced by an additional exposure in "print-out" emulsions. These specific "print-out" papers coated with a film, comprising a dispersion or emulsion of the compositions of the present invention, are particularly sensitive to a high intensity beam of light or other electromagnetic energy of either visible or invisible wave length exposed to a portion of the area of the film. While the material of the present invention is particularly sensitive to such exposure, the background or non-exposed area is sufficiently stable to render a highly contrasting image upon subsequent "latensification."

According to the present invention a photosensitive silver halide is used as the basic sensitive ingredient of the composition, the silver halide preferably being doped with a quantity of a compound selected from the class consisting of cadmium iodide and lead iodide in order to improve the photo response thereof. The photosensitive material is then dispersed in a quantity of hydroxyethyl starch, and other materials such as sensitizers or the like may be added if desired. The mixture is highly sensitive to brief exposures, in the range of microseconds from a high intensity source, but is substantially insensitive to relatively lower intensity radiations. A high degree of sensitivity to the trace beam coupled with a highly stable background, that is, a background which is not sensitive to a low intensity radiation, produces a maximum contrast between the image and the background, particularly when the material is utilized in recording operations. The present invention provides an unusual degree of sensitivity to high intensity radiations as well as an unusually high degree of insensitivity to low intensity radiations, thereby providing a highly sensitive trace recording paper having a particularly high degree of background stability.

The intensity of the radiation source utilized in latensification is not as critical with the sensitive mixtures of the present invention as it is with available compositions of the prior art. In other words, the accumulated quantity or intensity of illumination or radiation to which the sensitized paper is exposed during latensification is not particularly critical. The latensification rate obtainable by an intermediate intensity exposure to ordinary fluorescent lamp lighting conditions has been found to be satisfactory for the photosensitive silver halide compositions of the present invention, while this intensity of light is gen-

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erally less satisfactory for the available compositions and emulsions produced prior to the present invention.

The term "halide" as used throughout the specification is intended to encompass bromides, chlorides and iodides, fluorides being specifically excluded. Accordingly, various silver halides may be employed, silver halides consisting essentially or entirely of silver bromide being generally preferred.

In the early development of photography, "print-out" papers were relatively widely used for ordinary photographic purposes. With the advent of the improved development emulsions, "print-out" emulsions fell into a more and more limited use and this situation continued until only recently when it was recognized that they possessed desirable properties for high speed recording such as oscillographic recording and the like. As an example, such a recording system is disclosed in the co-pending application of Mahoney et al., Serial No. 638,729, filed February 7, 1957, and entitled "Recording Apparatus." Unfortunately, the sensitive papers and sensitive coating substances of the prior art are not entirely satisfactory for this recording purpose for a number of reasons. For example, it is generally true that the prior art papers which exhibit high sensitivity to an exposure of short duration to a high intensity beam tend to exhibit a correspondingly low degree of background stability. The printing out or latensification procedure for these sensitive papers is more critical, and accordingly it is difficult to carry out. The latent image may be entirely lost during the subsequent latensification operation due to the fact that the background "comes up" or "prints-out" too rapidly. In other cases a phenomenon known as "reversal" may occur, this being a darkening of the background which proceeds at a more rapid rate than darkening of the image or trace. In these situations, the trace may be temporarily or permanently lost. On the other hand, papers which exhibit a high degree of background stability tend to exhibit a correspondingly low degree of sensitivity to the recording beam and accordingly the maximum writing speed (minimum exposure time) is far below that desired for use with modern recording instruments. Hence, when it is attempted to produce a latent image upon a low sensitivity paper at an excessive rate for the paper, the image if formed at all will become lost against the background upon print-out.

In addition to these problems, it is also critical that the sensitive paper exhibit a certain degree of permanence in order that any record prepared thereon will have a sufficiently long and usable lifetime without losing its contrast. It is also desirable to have a sensitive paper which responds substantially uniformly to applied radiation without regard to certain inherent variations in intensities and writing speeds, and yet one which exhibits a substantially uniform degree of contrast against the background upon latensification under these conditions. According to the present invention, the sensitive films possess a sensitivity capable of writing in a wide range of speeds, including very slow speeds as well as speeds ranging up to more than 200,000 lineal inches per second. In spite of the varying requirements relative to different writing speeds, a uniform, relatively permanent and highly contrasting image is produced upon latensification. Latensification may be accomplished through exposure to radiation within the sensitive range for the paper for a very short period of time. For example, several seconds or less under an ordinary fluorescent lamp is sufficient to latensify or print-out certain images or traces made on paper prepared in accordance with the present invention.

Accordingly, it is an object of the present invention to provide improved "print-out" sensitive coating compo-

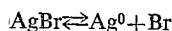
sitions which possess both a high degree of sensitivity to a trace recording along a portion thereof together with a high degree of background stability upon general latensification.

It is a further object of the present invention to provide improved "print-out" sensitive coating compositions which produce an image or trace which has a substantially uniform degree of contrast to the background, this contrast being relatively independent of the time the sensitive material has been exposed to a relatively intense trace source.

It is still a further object of the present invention to provide a photosensitive "print-out" coating composition which is exceedingly fast in its photographic response, which is substantially stable over a long period of time and which may be retained for an indefinite period of time so long as it is not exposed generally to relatively intense light or other electromagnetic radiation for extended periods.

It is yet another object of the present invention to provide an improved "print-out" emulsion which is dispersed in a quantity of hydroxyethyl starch, the dispersed mixture being readily and conveniently coated upon photographic paper.

The exact theory of operation of the compositions of the present invention is not entirely understood. In silver halides generally, and in particular silver bromide, exposure to light produces elemental silver and free halogen, this phenomenon probably being carried out in accordance with the reversible equation shown below.



Applied to the present case, the free silver indicates the exposed area and a darkening of the area occurs. When the light or other electromagnetic radiation is removed, the reaction in general may tend to reverse and therefore proceed to the left with a consequent loss of indicated exposed area. Silver halide emulsions have long been employed in the photographic art, including silver bromide and silver bromo-iodide as employed in the present invention. The presence of a composition selected from the group consisting of cadmium iodide and lead iodide is believed to prevent reverse reactions from occurring and hence the sensitivity is increased. A dispersion of this mixture in hydroxyethyl starch further enhances the background stability of the sensitive compositions as set forth hereinabove and renders it readily applicable to a base paper.

In accordance with the present invention, the photographic silver halide should preferably comprise about 80% (on a dry basis) of the finished composition, but for economical reasons, should generally not comprise substantially more than that amount. The cadmium and lead iodides should preferably be included in an amount ranging between about 1/2 and 20% in the case of cadmium iodide and from about 1/2% to 10% in the case of lead iodide. Good results are achieved with additions of about 5% of cadmium iodide and about 2% of lead iodide.

The compositions of the present invention may be further sensitized if desired, by adding from 0.01 to 0.2% (by weight based on total solids) of an organic sensitizer such as thiourea which is the preferred sensitizer for this composition. Thiocarbamide, thiosemicarbazide, paramethylamino phenol sulphate and mercapto succinic acid are useful and may be employed if desired.

The hydroxyethyl starch is essentially compatible with water, and if desired, thickening agents such as sea-weed extracts or polyvinyl alcohol may be employed.

The base paper or support, upon which the compositions may be spread or dispersed, may be almost any type of cellulose papers so long as it is free from macro size solid chips such as wood chips or the like. In this connection, conventional photographic base papers may be conveniently utilized.

For exposure and latensification, maximum sensitivity

of the paper is found to be below about 5,000 angstroms and mainly below about 4400 angstroms. Various commercially available high intensity light sources may be conveniently employed for producing the trace image, such as for example the Osram lamp manufactured by Osram, Munich, West Germany, and identified as their model HBO-107/1, high pressure mercury lamp. This lamp is employed as specified in the aforementioned application of Mahoney et al. By the term "high intensity radiation" reference is made to electromagnetic radiations having an intensity of about 10^8 ergs/sec./cm.² or greater. In order to obtain a useful trace, this radiation is applied to the material for a period of about 10^{-6} seconds or greater. Although somewhat lower intensity sources may be satisfactorily utilized, these sources may require substantially higher total exposure energy inasmuch as the material exhibits a strong low intensity reciprocity failure.

While the sensitive films are particularly sensitive to high intensity radiations, they may also be utilized at lower intensities, with a corresponding sharp drop in writing speed. For latensification, a less intense source of light is utilized generally across the extent of the paper. Ordinary fluorescent lighting at close range is useful both in its intensity and its total output wave-length characteristic for latensification operations. For example, latensification may be carried out under the influence of illumination of the order of 75 ft.-candles of "cool-white" fluorescent light.

In order to more particularly set out the features of the present invention, specific examples of preparation technique are presented hereinbelow:

EXAMPLE I

In accordance with the preferred embodiment of the present invention, the following preparation was prepared.

Preparation of Silver Nitrate Solution

Compound	Amount
AgNO ₃	170 gr. (1.0 mol).
H ₂ O (distilled).....	1,000 cc.
NH ₃ (23-30% aqueous solution, sp. gr. 0.90).....	400 cc.

The silver nitrate was weighed and dissolved in the prescribed amount of distilled water. Then the ammonia solution was added with stirring until the solution cleared as the precipitate of silver oxide formed by the first added portions of the ammonia was redissolved.

Potassium Halide Solution

Compound	Amount
KI.....	1.66 gr. (0.010 mol).
KBr.....	143 gr. (1.20 mol).
H ₂ O (distilled).....	300 cc.

The potassium iodide was weighed carefully in order to insure precise control over the iodide content of the resultant silver halide mixture. The potassium halides were dissolved in the prescribed amount of water contained in a two-liter beaker which was set in a water-ethylene glycol bath. The bath was heated on a hot plate to about 70°-80° C. The solution of potassium halide was stirred mechanically with a stainless steel stirrer.

Preparation of Silver Bromo-Iodide

When the halide solution was hot (70 to 80° C.) the ammoniacal silver nitrate solution was added slowly in a steady stream to the reaction vessel. This was done by pouring the silver solution slowly into a funnel to the outlet of which has been fused a short length (about 4 inches) of capillary tubing. The capillary jet delivered the silver solution at a rate of about 30 cc. per minute,

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so that the addition of silver was completed in about 50 minutes. While the iodide reacts preferentially because of its being less soluble than the silver bromide, there may be considerable co-precipitation so that silver iodide is trapped in silver bromide crystals with the result that strained crystals of high sensitivity are formed.

Ammonia and potassium bromide act as solvents for the silver halides formed and promote crystal growth. Thus, in the presence of these solvents, the smaller silver halide crystals may dissolve and be re-deposited on the surfaces of larger crystals by a process known as Ostwald ripening. This process can occur during the slow precipitation step. The mixture was stirred vigorously with a mechanical stirred during the precipitation period.

After the precipitation step, the silver halide mixture was filtered by suction on a Buchner funnel and was washed five times with distilled water. It is not normally necessary to dry the silver halides after filtering and washing.

In addition to the silver bromo-iodide, cadmium iodide was employed to increase the print-out effect and to assist in suppressing background during latensification.

Compound	Amount
Silver Halide (as prepared hereinabove).....	100 gr.
Cadmium Iodide.....	5 gr.
Water (distilled).....	50 cc.
Hydroxyethyl Starch (30% hydroxyethyl starch in water solution).....	67 gr.

The ingredients listed above with the exception of the hydroxyethyl starch solution were placed in a pint porcelain jar of a ball mill containing 200 grams of one-half inch porcelain pebbles. The bottle was rotated at about 60 r.p.m. for a period of one hour. The hydroxyethyl starch was then added and the mixture ball-milled for another one hour, after which time a homogeneous mixture resulted. The mixture described above had a consistency which was found readily adaptable for making flow-coated papers.

In this connection various application techniques may be employed, such as transfer roller coating, dip coating using an air-knife to wipe off the excess upon emergence from the bath, or by conventional spreading using a doctor knife to control the thickness of the film. Although the thickness of the coatings to be applied to paper or other supports is dependent on the characteristics desired in the end product, it has been found that the composition disclosed above was then applied in layers calculated to be in the range of about 0.5 mil in thickness were useful. As the thickness of the wet film is difficult to measure, it is somewhat easier to use the weight per unit area of solids deposited as a reference. About 1 gram of solids per square foot of the dried film appears to be satisfactory. The critical features are that the coating be uniform, flexible, and adherent to the base material. After application to the base plate, the coating was permitted to dry.

The sensitive material prepared in accordance with Example I hereinabove was yellow in color, and upon the desired exposure to light, a uniform medium dark brown image or trace having extremely uniform and fine edged definition was formed. Sensitive papers prepared according to this process were capable of writing speeds equivalent to more than 200,000 inches per second when illuminated from a source having an intensity of about 100,000 candles per square centimeter under the spectrum distribution obtainable from the Osram lamp described hereinabove, the lamp being employed as specified in the aforementioned application of Mahoney et al. A high proportion of this radiation is in the ultraviolet range of the spectrum. A complete system for recording is described and disclosed in the aforementioned Mahoney et al. application. In printing out, subsequent to formation of the latent trace the sensitive paper was exposed to low intensity ambient light in the range of 50 to 75 foot-candles of fluorescent radiation for about two minutes.

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At this time, traces prepared at speeds less than about 50,000 to 70,000 inches per minute were prominent and clearly visible. It appears that during this period the background was fixed, and prolonged exposure to ambient light was possible without appreciable adverse effects. After low intensity post exposure, the paper was exposed to strong ultraviolet radiation for some minutes. Sunlight, high pressure or low pressure mercury lamps may be utilized for this purpose. During this exposure, the trace darkens considerably with the background darkening only slightly. In addition, at this time, traces prepared at speeds from 75,000 to 200,000 inches per second become prominent.

EXAMPLE II

The silver halide mixture was prepared as in Example I. In addition to the silver bromo-iodide, lead iodide was employed to increase the print-out effect and to assist in suppressing background during latensification.

Compound	Amount
Silver Halide.....	100 gr.
Lead Iodide.....	2 gr.
Water (distilled).....	50 cc.
Hydroxyethyl Starch (30% hydroxyethyl starch in water solution).....	67 gr.

The ingredients listed above with the exception of the hydroxyethyl starch binder solution was placed in a pint porcelain jar of a ball mill containing 200 gr. of one-half inch porcelain pebbles. The bottle was rotated at a speed of 60 r.p.m. for a period of one hour. The hydroxyethyl starch binder solution was then added and the mixture ball-milled for another hour, after which time a homogeneous mixture resulted. The mixture described above had a consistency which was found readily adaptable for making flow coated papers.

The mixture was coated on paper by means of transfer roller coating to a thickness of about 0.5 mil. The coating was uniform, flexible and adherent to the base paper.

This sensitive material was yellow in color and upon exposure to light, a uniform medium dark-brown image or trace having extremely uniform and fine edge definition was formed. Sensitive papers made in accordance with Example II were found capable of writing at speeds in the range of 50,000 inches per second when illuminated from a source having an intensity of about 100,000 candles per square centimeter under the spectrum distribution obtainable from the Osram lamp described hereinabove in connection with Example I.

It will be appreciated from the foregoing description that the present invention makes possible the production of sensitive papers capable of giving a sharp visible image at writing speeds of up to 200,000 inches per second. The latent image becomes more visible a short time after exposure to fluorescent light, and maintains extremely good contrast against background for extended periods of time. Such papers obviously find extensive use in modern recording instruments.

Other and further modifications may be employed without departing from the spirit and scope of the present invention. It will be appreciated, of course, that the foregoing examples are given for purposes of illustration and there is a accordingly no intention to limit the scope of the present invention to these particular modifications alone.

I claim:

1. A photosensitive "print-out" composition comprising a mixture of a washed precipitated silver halide from the class consisting of silver bromide and silver bromo-iodide, doped by addition of a doping agent from the class consisting of lead iodide and cadmium iodide, said doping agent being from 0.5 to 20% by weight of said silver halide for cadmium iodide and from 0.5 to 10% by weight of said silver iodide for lead iodide, said mixture being dispersed in a suspension of hydroxyethyl starch.

2. A photosensitive "print-out" composition comprising a mixture of washed precipitated silver halide from the class consisting of silver bromide and silver bromo-iodide, doped by addition of from $\frac{1}{2}$ to 20% by weight of said silver halide cadmium iodide, said mixture being dispersed in a suspension of hydroxyethyl starch.

3. A photosensitive "print-out" composition comprising a mixture of a washed precipitated silver halide from the class consisting of silver bromide and silver bromo-iodide, doped by addition of from $\frac{1}{2}$ to 10% by weight of said silver halide lead iodide, said mixture being dispersed in a suspension of hydroxyethyl starch.

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