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PHOTOSENSITIVE SYSTEM

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15 Claims. (Cl. 96—90)

This invention relates to a photochemical process and product and, more particularly, to a photosensitive system based on a combination of a colorless dye cyanide with a collagenous protein.

In my application, Serial No. 542,479, filed October 24, 1955, I have disclosed that hydrophilic dye cyanides form photosensitive combinations with hydrocolloids, generally. In this application, I pointed out the great advantages of that type of photosensitive system over those obtained by combining colorless dye cyanides with the previously known activators.

I have also discovered that a particular type of hydrophobic dye cyanide may be combined with a particular type of hydrocolloid and obtain these same advantages.

Thus, it is a primary object of the present invention to provide a solid composition including a triphenylmethane dye cyanide of long shelf life which is activated by a nonvolatile and solid organic material so as to be sensitive to ultra-violet light.

A further object of the invention is to provide a photosensitive composition capable of forming films which may be either self sustaining or coated over a suitable supporting base and which are printing out materials of execeptionally high speed and resolution.

Another object of the invention is to provide a photosensitive combination on which images printed by means of ultra-violet irradiation are permanent and do not fade in the dark, and retain their fine detail indefinitely.

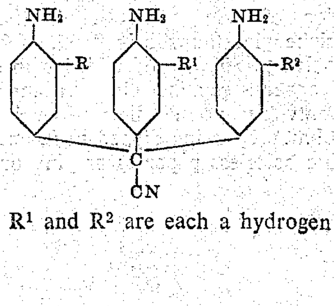
Still another object of the invention is to provide an activated triphenylmethane dye cyanide composition sensitive to ultra-violet light from which there will be no diffusion of the activator.

Yet another object of the invention is to provide an activated triphenylmethane dye cyanide composition sensitive to ultra-violet which is less subject to injury by contact with various deleterious substances such as rosin in sized papers and phthalates in plasticized plastics.

Another object of the invention is to provide a photochemical process which utilizes a composition which accomplishes the foregoing objects.

Other and further objects of the invention will be apparent from the folowing detailed description.

I have found that the collagenous proteins form with one class of the simple basic triphenylmethane dye cyanides, combinations or compounds sensitive to ultra-violet and shorter wave lengths. This particular class is the tri-primaryamino triphenylacetonitriles and the compounds represented by the general formula



in which R, R^1 and R^2 are each a hydrogen atom or a methyl group, are all suitable for use in the present invention, singly or in admixture.

Of the four compounds embraced within this formula, 4,4′,4″ - triamino - triphenylacetonitrile and its 3-methyl derivative are preferred because of their ready availability, but the 3,3′ - dimethyl derivative and 3,3′,3″ - trimethyl derivative also form quite satisfactory photosensitive combinations with collagenous proteins.

The photosensitive combination or compound formed between the collagenous proteins and the simple, hydrophobic, basic dye cyanides appears to be specific to the primary amono substituted triphenylacetonitriles. It is not formed to any practical extent by the completely alkylated derivatives such as 4, 4′,4″ - tris - dimethylamino-triphenylacetonitrile, or 4,4′ - bis - dimethyl - amino - triphenylacetonitrile.

Suitable collagenous proteins for use in the invention are the gelatines obtained from calfskin, pigskin, hooves, and the like and the glues, such as fish glues and the animal glues obtained from hides and hooves. The individual gelatines and glues may differ considerably in their properties but all have been found to provide suitable photosensitive combinations with the indicated dye cyanides.

The nature of the combination of the dye cyanide with the collagenous protein has not been clearly established, but the combination has some of the properties of a dyed material. For example, if a film formed of gelatine combined with one of the triprimaryamino-triphenylacetonitriles is soaked in cold water, it swells and forms swollen flakes of clear colorless gelatine. If the mixture is centrifuged and exposed to ultra-violet radiation the gelatine flakes become strongly colored while the aqueous layer remains colorless, showing that the dye cyanide is still in activated combination with the gelatine and has not been precipitated and deactivated by the addition of water.

The method of combining the dye cyanide with the collagen material is not critical as it is only necessary that the dye cyanide be brought into intimate contact therewith so that a photosensitive combination results. Thus the collagen material may be in solid or liquified form during the formation of the photo-sensitive combination and one method employing the collagen derivative as a solid delineates the analogy between the combination and a dyed material. Gelatine in its granular form of commerce may be stirred in a solution of dye cyanide salt cooled to a temperature (e. g. 0° C.) which prevents dissolution of the gelatine, separated from the solution and washed with cold water. The gelatine may then be liquified by heating with the desired amount of water and used as coating material to yield smooth and colorless films which are sensitive to ultra-violet and shorter wave lengths. It will be apparent that the gelatine has extracted the dye cyanide from solution much as textiles will extract dyes in the processing of dyeing.

Another convenient method of forming the photosensitive combination is to mix an aqueous solution of the collagenous protein at a temperature at which it is liquid with a solution of the basic dye cyanide in an organic solvent, such as i-propyl alcohol or acetonitrile, which is tolerated in considerable proportions by the collagen solution without precipitation of the collagen. The resulting mixture may then be used to coat or impregnate a suitable base material and the solvent evaporated. The resulting dry product is strongly sensitive to ultra-violet and shorter wave lengths to produce a magenta color.

One particularly advantageous method of forming the present photosensitive combinations makes use of the increased solubility in water and hydrophilic organic solvents of the salts of the basic dye cyanides which are suitable for use in the present invention, thus facilitating their admixture with a solution of the collagenous protein. In accordance with this process, an aqueous solution of the collagenous protein at an elevated temperature is mixed with a solution of a salt of the dye cyanide.

The use of acid in this method has the added advantage that the presence of acid in addition to the basic dye cyanide and collagenous protein leads in general to more sensitive preparations than the combination of collagenous protein and dye cyanide in the form of its base alone. I have found it generally satisfactory to employ acid in the ratio of one equivalent to three equivalents of acid per molecule of dye cyanide. The use of less acid does not provide the advantages sought; whereas the use of more than three equivalents of acid per molecule of dye cyanide, although it does not prevent the formation of a photosensitive film, results in unnecessary degradation of the protein and gives a product that is inferior in physical qualities.

The acid employed may be a mineral acid or an organic acid, it being only necessary that the acid belong to the group referred to as "strong" acids. That is to say, the acid should have a dissociation constant for the first hydrogen greater than 10^{-4}. As examples of such acids there may be named hydrochloric, sulfuric, perchloric, dichloracetic, trichloracetic, benzene sulfonic, p-toluene sulfonic, formic and oxalic.

While it is preferred that the acid be introduced into the photosensitive combination in the form of a salt of the dye cyanide, it is to be understood that it can be added in any other suitable manner.

Regardless of the method of forming the photosensitive combination, its solutions lend themselves excellently to the preparation of coated and impregnated materials which have a number of important uses, for example, coated glass plates may be used for the preparation of lantern slides and other transparencies which can be projected or examined by visible light without any fixing process and without destroying the ultraviolet photosensitivity. Likewise, cellulose acetate and similar films may be coated to make transparent photosensitive materials.

Papers may also be coated, and, for example, Baryta coated photographic raw stock, when coated with a film of the composition of this invention affords an opaque photosensitive sheet that prints rapidly to give a brilliant image.

The collagenous protein-triaminotriphenylacetonitrile combination is capable of giving films of extremely high resolution so that images will show microscopic detail. These films have no grain like a silver emulsion, and are transparent and uniform under a microscope. The images formed have the property of being as sharp as the beam of light producing the image. Where the image is projected by a lens or other focusing device, maximum resolution is obtained by making the photosensitive film very thin so that it may be placed at the exact focus at which the image is formed and thus hold to a minimum the sidewise diffusion of the image as the light passes through the film.

The relative proportion of dye cyanide to collagenous protein in the photosensitive combination is not critical and must necessarily vary widely in accordance with such factors as the viscosity of the protein solution employed in preparing the combination and the thickness of the dried films to be formed therefrom. In general, the amount of dye cyanide should be kept as low as possible consonant with the formation of clear, deeply-colored images. In most instances, the proportion of dye cyanide will fall within the range of 0.1 to 10.0% based on the weight of the dried photosensitive combination.

Expressing the amount of dye cyanide in terms of the exposable surface area of the photosensitive product, it has been found that there may be from .01 to 10 mgms. of dye cyanide per square inch of surface.

The following examples are set forth as being illustrative of, but not as limiting, the invention.

Example 1

One volume of a 10% aqueous solution of purified calfskin gelatine is mixed at 45° C. with ½ volume of a ¼ of 1% solution of 4,4',4''-triamino-triphenylacetonitrile in acetonitrile. The resulting mixture is poured onto level glass plates which are dried in the dark in a dust free atmosphere. Exposure of the dried film to 10,000 ergs per square centimeter of 2537 A. radiation prints out a good magenta image which has good resolution and does not fade in the dark.

Example 2

One gram of 4,4',4''-triamino-triphenylacetonitrile is dissolved at room temperature in 9.6 ml. of normal hydrochloric acid and the solution diluted to 100 ml. with water, to give approximately 1% dye cyanide dissolved as the trihydrochloride. A sensitizing mixture is made of 10 ml. of the above solution, 20 ml. of water, 30 ml. of 10% gelatine and 30 ml. of 91% i-propyl alcohol, all at 50° C. The mixture is cooled to 35° C. and used to impregnate 24 lb. water leaf paper, which is air dried in the dark. This paper gives usable images over the exposure range of 2,000 to 1,000,000 ergs per square cm. of total radiation of wave lengths 3132 A. and shorter from a hot quartz mercury lamp.

Example 3

10 ml. of the approximately 1% dye cyanide solution as trihydrochloride prepared in Example 2 is mixed with 30 ml. of water and 20 ml. of photo-engraver's glue (e. g. Roger's Photoengraver's Glue). Water leaf paper is impregnated with this mixture and dried in the dark to give a material sensitive to radiation shorter than 3250 A. The sensitizing mixture may also be applied to paper or cloth with a brush through a stencil to give photosensitive designs.

Example 4

Twenty-five grams of Magenta ABN (General Dyestuffs Corp.) is dissolved in 350 ml. of boiling water, the solution cooled to 45° C., filtered, and the filtrate treated with a solution of 5.3 g. of 95% sodium cyanide in 25 ml. of water. Reaction begins immediately with precipitation of the new compound. The reaction mixture is allowed to stand in the dark at room temperature for 12 hours, and the following operations carried out by yellow light. The reaction product that has precipitated is collected on a filter, washed on the filter with 1000 ml. of water, and air dried at 50° C.

Purification is carried out as follows: Ten grams of the dry crude product is dissolved by stirring at 25° C. in a mixture of 75 ml. of triethyl phosphate and 25 ml. of water. The solution is filtered and put in a 400 ml. beaker and stirred while water is added drop by drop at the rate of 2 ml. per hour until a total of 100 ml. of water has been added. The nearly colorless crystalline precipitate of 4,4',4''-triamino-3,3',3''-trimethyl-triphenylacetonitrile is collected on a filter, washed with water until the wash is colorless, and dried in a vacuum desiccator over sulfuric acid. A second crop of slightly less pure material may be obtained by treatment of the mother liquor with 700 ml. more water added all at once.

A solution of 0.05 g. of 4,4',4''-triamino-3,3',3''-trimethyl-triphenylacetonitrile in 4 ml. of boiling acetonitrile is cooled to 50° C. and added with stirring to 34 ml. of 10% aqueous gelatine solution at the same temperature. Twenty-four pound filter paper is impregnated with this solution by being dipped in it, and is air dried. The resulting colorless paper turns pink on exposure to ultra-violet.

Example 5

A solution of rosaniline cyanide mono-p-toluene sulfonate is made by heating together 0.1 g. of 4,4′,4″-triamino-3-methyltriphenylacetonitrile, 0.058 g. of p-toluene sulfonic acid monohydrate and 10 ml. of 99% i-propyl alcohol until the alcohol boils. When the solids have dissolved the solution is cooled to 50° C. and mixed by stirring with a solution at the same temperature of 5 g. of gelatine in 85 ml. of water. The resulting mixture is coated onto glass plates, using ½ ml. per square inch of surface, which are dried in the dark. The resulting film prints out a magenta image on exposure to ultra-violet.

Example 6

At room temperature 0.3 g. of 4,4′,4″-triamino-triphenylacetonitrile is dissolved in 2.85 ml. of normal hydrochloric acid by stirring for a few hours in the dark or yellow light. The rest of the preparation is also carried out by yellow light. The solution is diluted with water to 200 ml. and cooled to 0° C. 10 grams of granular U. S. P. gelatine is added and the mixture stirred at 0° C. for 1½ hours. The mixture is then made up to a volume of 500 ml. with ice water, allowed to settle for 15 minutes, and the supernatant cloudy solution decanted from the gelatine, which is washed three times in the same way with 500 ml. portions of ice water. When the last wash has been decanted the gelatine suspension, which has a volume of about 150 ml. is liquified by heating to 100° C. in a water bath and used to coat glass plates with 2 ml. per square inch of surface. The dried films are colorless and smooth, though with a slight grain, and become magenta on exposure to ultra-violet radiation of wave length shorter than 3300 A.

Example 7

In yellow light 0.6 g. of 4,4′,4″-triaminotriphenylacetonitrile is dissolved by stirring at room temperature in 5.7 ml. of normal hydrochloric acid and the solution made up to 180 ml. of water. To this solution is added 480 ml. of i-propyl alcohol and 10 g. of granular U. S. P. gelatine, and the mixture is stirred at 20° C. for 9 hours. The gelatine is then allowed to settle. The clear supernatant solution is decanted and the gelatine washed twice with 100 ml. portions of i-propyl alcohol. Water is then added to the drained gelatine to a total volume of 150 ml. The gelatine is liquified by heating the mixture to 100° C. in a water bath, and glass plates are coated, using 2 ml. of solution per square inch of glass surface. The film dries colorless and completely clear, and prints grainless images on exposure to ultra-violet.

Example 8

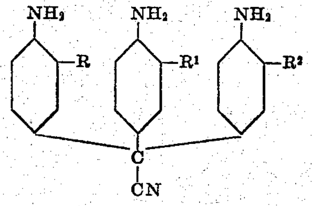
By yellow light, 0.3 g. of 4,4′,4″-triamino-3-methyl-triphenylacetonitrile and 0.175 g. of p-toluene sulfonic acid mono-hydrate are dissolved in 30 ml. of boiling i-propyl alcohol, the resulting clear solution cooled and made up to 40 ml. with water. At 20° C. 5 g. of granular U. S. P. gelatine is added and the mixture stirred at this temperature for 2 hours. The gelatine is allowed to settle, the supernatant solution decanted, and the gelatine washed twice with 100 ml. portions of i-propyl alcohol. The drained gelatine is made up to 75 ml. with water, dissolved by heating to 100° C. on a water bath and used to coat barium sulfate coated paper. The dry coated paper prints out a magenta image on exposure to ultra-violet.

In the above preparations all solutions containing a triaminotriphenylacetonitrile, and its combinations with a collagenous protein, should be protected from ultra-violet radiation and handled preferably by yellow light such as is suitable for the processing of silver developing out paper.

I claim:

1. A solid composition photosensitive only to ultra-violet and shorter wave lengths, consisting of a combination of a collagenous protein and a triprimaryamino-triphenylacetonitrile.

2. A solid composition photosensitive only to ultra-violet and shorter wave lengths, consisting of a combination of a collagenous protein and a colorless dye cyanide having the general formula



wherein R, R^1 and R^2 are each selected from the group consisting of a hydrogen atom and a methyl group.

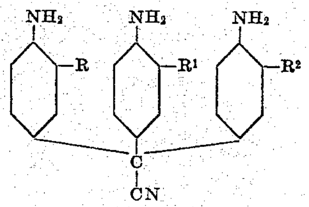
3. The photosensitive composition of claim 2 in which said protein is a gelatine.

4. The photosensitive combination of claim 2 in which said protein material is a glue.

5. The photosensitive composition of claim 2 in which said dye cyanide is 4, 4′, 4″-triamino-triphenylacetonitrile.

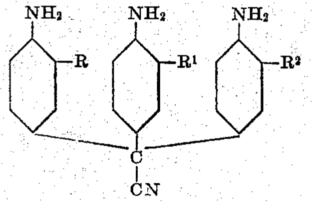
6. The photosensitive composition of claim 2 in which said dye cyanide is 4, 4′, 4″-triamino-3-methyl-triphenylacetonitrile.

7. A solid composition photosensitive only to ultra-violet and shorter wave lengths, consisting of a combination of a collagenous protein, a colorless dye cyanide having the general formula



wherein R, R^1 and R^2 are each selected from the group consisting of a hydrogen atom and a methyl group and 1 to 3 equivalents of an acid having a dissociation constant for the first hydrogen greater than 10^{-4} for each molecule of said dye cyanide.

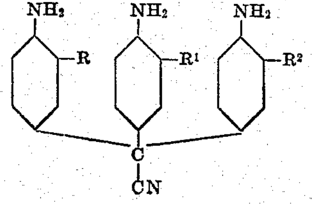
8. A product of manufacture comprising a base sheet coated with a solid composition photosensitive only to ultra-violet and shorter wave lengths, said composition consisting of a combination of a collagenous protein and a colorless dye cyanide having the general formula



wherein R, R^1 and R^2 are each selected from the group consisting of a hydrogen atom and a methyl group.

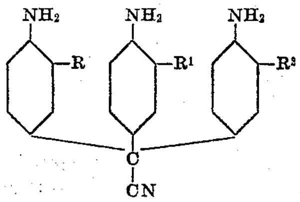
9. The product of claim 8 in which said collagen material is a gelatine.

10. A product of manufacture comprising a base sheet coated with a solid composition photosensitive only to ultra-violet and shorter wave lengths, said composition consisting of a combination of a collagenous protein, a colorless dye cyanide having the general formula



wherein R, R^1 and R^2 are each selected from the group consisting of a hydrogen atom and a methyl group and 1 to 3 equivalents of an acid having a dissociation constant for the first hydrogen greater than 10^{-4} for each molecule of said dye cyanide.

11. A photochemical process comprising exposing to ultra violet light to produce a colored compound, a solid composition consisting of a combination of a collagen material and a colorless dye cyanide having the general formula



where R, R^1 and R^2 are each selected from the group consisting of a hydrogen atom and a methyl group.

12. The photosensitive composition of claim 7 in which said dye cyanide is 4, 4′, 4″-triamino-triphenylacetonitrile.

13. The photosensitive composition of claim 7 in which said dye cyanide is 4, 4′, 4″-triamino-3-methyl-triphenylacetonitrile.

14. The photosensitive composition of claim 7 in which said dye cyanide is 4,4′,4″-triamino-3,3′,3″-trimethyltriphenylacetonitrile.

15. The photosensitive composition of claim 2 in which said dye cyanide is 4,4′,4″-triamino-3,3′,3″-trimethyltriphenylacetonitrile.

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