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PROCESS OF COLORING PHOTOGRAPHIC IMAGES

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My invention relates in general to the art of color photography, with particular reference to a new and novel method for producing a Prussian Blue photographic image suitable for use in motion pictures. While the process of my invention is applicable to both still and motion picture photography, it finds its widest range of application in the latter branch of the art, and consequently, I will confine this description of a preferred form of my invention to its adaptation in motion picture transparencies, it being understood that whenever the term "film" is used, it is meant to include all types of film, photographic plates, and paper for all branches of photography.

In producing colored pictures by subtractive methods, one of two types of film is generally used; first, a film which comprises a base with a layer of emulsion upon each side thereof, or second, a film comprising a base with a layer of emulsion upon only one side thereof, which said layer may have the same sensitivity throughout, or may have a varying or stratified sensitivity, depending upon the use to which it is to be put. In producing positive prints in color, by the use of film having an emulsion layer on one side only, it is usual to have the emulsion sensitized substantially uniformly throughout, one photographic color-value image being produced in the upper or outer stratum of the emulsion layer by printing from a negative to the face of the emulsion, and a second photographic image of another color-value is printed or produced in the lower or inner stratum by printing through the base from another color-value negative. If the process is a two color process, this constitutes the entire printing step, however, if a three-color process is being followed various methods may be employed for producing three images in the emulsion layer, either by printing as aforesaid or by imbibing, or by a combination of the two. If a double emulsion film is being used, two images may be produced on one side of the base and a third image on the opposite side.

It is the major object of my invention to provide a process of color photography whereby a satisfactory blue-toned image can be produced in the outer stratum of an emulsion layer without contaminating or in any way destroying an inner photographic image already present in the inner stratum of said emulsion layer, which said inner image can therefore subsequently be colored a different color by any one of various convenient means.

I am aware of the fact that various color processes have been promulgated which utilize a single emulsion film, place two images in separate strata thereof, and color the images substantially complementary colors. I have found, however, that it is very difficult to control the treatment of two images in separate strata of the same emulsion layer so as to produce separate colored images which are satisfactory since in the usual known processes of this type, the step or steps which are used in coloring the outer image usually affect the inner image to its detriment, or yield an outer image which is subsequently modified or otherwise damaged by the treatment prescribed for the inner image, this being particularly true when it is attempted to produce a Prussian Blue image in the outer stratum and a red image in the inner stratum. It, therefore, becomes an object of my invention to provide a process whereby the production of a Prussian Blue image in the outer stratum of an emulsion layer can be accurately controlled both as to penetration and quality.

In the preferred practice of my invention, I produce a blue color-value image in the outer stratum of a single emulsion layer, and a red color-value image in the inner stratum of said layer by any suitable means, such as above mentioned, these images being developed and fixed in the usual manner so that they both comprise free silver, although it will be understood of course that my invention comprehends the production of a silver image in the surface or outer stratum without producing an image in the inner stratum until after the outer image has been converted to Prussian Blue.

The first step in treating the outer or surface image to transform it into a Prussian Blue image comprises converting it into an insoluble silver salt which can be converted into silver ferrocyanide by subsequent treatment with a solution of a soluble ferrocyanide. The preferred salt of this type is silver chloride which is obtained by treating the silver image with an acidified solution containing ferric ions and chloride ions. To produce the silver chloride image, I prefer to use an acidified solution of ferric chloride in alcohol or some other slow-penetrating solution. By using ferric chloride both the ferric and chloride ions are obtained from the one salt and by using alcohol as a solvent the rate of penetration of the solution is kept down to a minimum. Other substances can, of course, be used for producing the ferric and chloride ions, such for instance as ferric sulphate an hydrochloric acid. Likewise, if for any reason it is not desired to use alcohol as a solvent, a salt such as magnesium or alu-

minum sulphate which can be made into a comparatively concentrated solution may be used to retard and control the rate of penetration of the ferric and chloride ions. In this connection, I have found that a sugar solution can be used in place of salt with a similar action, although none of these alternative forms have proven quite as satisfactory as alcohol. By this means it is possible to provide a bleaching solution which penetrates very slowly and which therefore can be accurately controlled so that the outer image can be completely treated without affecting the inner image, whereas, if it is attempted to tone the outer image blue, in the customary manner it will be found that the solution penetrates very rapidly and accurate control is very difficult. I have also found that the introduction of substances into the ordinary iron toning solution for the purpose of retarding the rate of penetration has not proven satisfactory in that the blue toning solution usually breaks down or becomes inactive. However, when using a solution such as ferric chloride as the first step in the treatment of the image, it is possible to incorporate in the solution a retarding substance such as previously mentioned, or to create a slow penetrating solution of the chloride by dissolving it in alcohol, neither of which procedures in any way lowers the efficiency of the bleaching solution.

After the image in the outer stratum of the film has been treated for a suitable time with the chloride bleach, further penetration of the bleach is stopped in any convenient manner, such as by immersion in a 2.5% solution of potassium oxalate which reacts with the excess ferric chloride present and also with the ferrous chloride to some extent, to form an inactive complex salt which is soluble and can be washed out of the film. By this procedure, the excess ferric ions are removed from the gelatin so that further penetration thereof and reaction with any silver image that may be in the lower stratum is prevented. Following the stop bath, the film is thoroughly washed to remove the complex iron salts and the ferrous chloride, leaving an image of silver chloride in the outer stratum of the film. This silver chloride image is then converted to a silver ferrocyanide image by treatment with a suitable ferrocyanide, such as a 2% solution of potassium ferrocyanide. This treatment is usually allowed to continue for approximately 3 minutes and is followed by a wash for about 3 minutes, which removes the potassium chloride, formed by the reaction, and any excess potassium ferrocyanide which may be present. While I prefer to use potassium ferrocyanide I have found that any soluble ferrocyanide such for example as sodium ferrocyanide and ammonium ferrocyanide can be used in my process with satisfactory results.

The silver ferrocyanide image is now converted to ferrous ferrocyanide, with a solution containing ferrous ions and halide ions, such for example as a solution of 3% ferrous chloride and 5% potassium iodide which solution has no oxidizing action on the inner image. Ferrous chloride, iodide, or bromide may also be used in conjunction with a soluble halide, the principal consideration being to provide ferrous ions and halide ions in the solution, so that the halide ions can displace the ferrocyanide ions from the silver ferrocyanide, leaving the ferrocyanide free to combine with the ferrous ions to form ferrous ferrocyanide. This treatment is also followed by a water wash for approximately 3 minutes, which removes the excess ferrous halide and the potassium chloride formed, leaving an image of ferrous ferrocyanide and silver halide in the outer stratum.

The film is then treated with a suitable oxidizing solution such as a neutral 1% potassium dichromate solution which oxidizes the ferrous ferrocyanide to ferric ferrocyanide or Prussian Blue. While I prefer to use potassium dichromate as the oxidizing agent, I have found that there are a number of suitable agents for this purpose, such for example as sodium dichromate, hydrogen peroxide, or some other oxidizing agent which will oxidize ferrous ferrocyanide to ferric ferrocyanide without oxidizing the free silver in the inner image. After the Prussian Blue image has been formed, the film is washed thoroughly, and then the silver halide is removed from the blue image by fixing in a suitable solution such as a strong sodium thiosulphate solution, followed by a water wash of approximately 4 minutes, which results in a transparent Prussian Blue image which is very satisfactory for motion picture projection purposes.

The film can now be treated in any convenient manner to provide the second colored image which in a two-color process will be substantially complementary to the outer Prussian Blue image.

If a three-color process is being employed, so that three color-separation images or color-value images are to be produced, they can be provided in a number of ways. For instance, an extra thick emulsion can be employed so that three separate images can be formed in three separate strata of the emulsion and after the outer image has been blue-toned by the process described above, the other images can be colored magenta and yellow respectively by suitable processes. However, for three-color work, I prefer to utilize the ordinary emulsion which is suitable for carrying two images in separate strata and after coloring the outer image blue by the herein-described method, I color the inside image red by either toning with uranium or copper, or bleaching with iodine and then dyeing the image magenta with any suitable basic dye. The yellow image can then be imbibed on the film in the usual manner giving a resultant three-color photograph without the necessity of employing special emulsion layers or having to minutely control the treatment of superposed images in the same emulsion layer, which is always a source of difficulty.

It will be understood, of course, that my process is applicable to sound films and that where I use the term "image," I mean to include sound track images as well as picture images.

While I have given particular formulas throughout for the preferred practicing of my invention, it is to be understood of course that certain modifications can be made in the ingredients and in the proportions of said formulas without departing from the scope of my invention, and it is to be understood that the foregoing description is not to be taken as limiting but is merely to be considered as illustrative of the broad principles of my invention as defined in the appended claims.

I claim as my invention:

1. The process of producing a Prussian Blue image from a photographic silver image which includes: converting said silver image into an insoluble silver salt capable of being converted to silver ferrocyanide; converting said image thus formed to silver ferrocyanide; converting said silver ferrocyanide image to ferrous ferrocyanide;

and oxidizing said ferrous ferrocyanide image to ferric ferrocyanide.

2. The process of producing a Prussian Blue image from a photographic silver image which includes: converting said silver image into a silver halide image; converting said image thus formed to silver ferrocyanide; converting said silver ferrocyanide image to ferrous ferrocyanide; and oxidizing said ferrous ferrocyanide image to ferric ferrocyanide.

3. A process as defined in claim 2 in which said silver image is converted to a silver chloride image.

4. The process of producing a Prussian Blue photographic image from a silver image which includes: treating said silver image with a solution containing ferric ions and halide ions; treating the resultant image with a solution of soluble ferrocyanide; converting said image thus formed to ferrous ferrocyanide; oxidizing the resultant image to ferric ferrocyanide; and removing the silver salt present in said image.

5. A process as defined in claim 4 in which said first treating solution contains ferric chloride.

6. A process as defined in claim 4 in which said first treating solution contains ferric chloride dissolved in alcohol.

7. A process as defined in claim 4 in which said first treating solution is an acid solution of ferric chloride in alcohol.

8. The process of producing a Prussian Blue photographic image from a silver image which includes: treating said silver image with an acid solution containing ferric chloride, to produce a silver chloride image; converting said silver chloride image to silver ferrocyanide by treatment with a soluble ferrocyanide; treating said silver ferrocyanide image with a solution containing ferrous ions and a soluble halide; and converting the image thus formed to ferric ferrocyanide.

9. A process as defined in claim 8 in which said first treating solution contains an agent adapted to retard the penetration of said solution into said image.

10. A process as set forth in claim 8 in which the conversion of the silver ferrocyanide image to ferrous ferrocyanide is accomplished by treatment with a solution containing ferrous chloride and a soluble iodide.

11. The step in a method of producing a colored photograph which includes: producing a silver color-value image in the outer stratum of an emulsion layer; treating said film with a relatively slow penetrating acid solution containing ferric and halide ions; arresting the action of said treating solution; converting the image thus formed to silver ferrocyanide; converting said silver ferrocyanide image to ferrous ferrocyanide and then to ferric ferrocyanide; and removing the silver halide from said image.

12. A method as defined in claim 11 in which the first treating solution is an alcoholic solution of ferric chloride.

13. A method as defined in claim 11 in which the first treating solution is an acid solution of ferric chloride in alcohol.

14. The method of treating a photographic silver image which includes: treating said image with an acid solution of ferric chloride in alcohol; arresting the action of said solution by immersing said image in a suitable stop bath; treating the silver chloride image thus formed with a solution of potassium ferrocyanide; converting the resultant silver ferrocyanide image to ferrous ferrocyanide by treatment with a solution containing ferrous chloride and potassium iodide; oxidizing said image to ferric ferrocyanide; and removing the silver iodide from said image by treatment with a strong sodium thiosulphate solution.

15. A process as defined in claim 14 in which the oxidizing agent is potassium dichromate.

16. The method of producing a colored photograph in a single emulsion which includes: producing a silver color-value image in the outer stratum of said emulsion; converting said image to silver chloride; treating said image with a soluble ferrocyanide; converting the image thus formed to ferrous ferrocyanide; oxidizing said image to ferric ferrocyanide; and producing a substantially complementary-colored image in the inner stratum of said emulsion in register with said first image.

17. A method as defined in claim 16 in which the conversion of said silver image to silver chloride is accomplished with a relatively slow-penetrating solution.

18. A method as defined in claim 16 in which the silver chloride image is obtained by treatment with an acid alcoholic solution of ferric chloride.

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