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PROCESS AND TREATING BATH FOR THE PRODUCTION OF COLORED PHOTOGRAPHIC PICTURES

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In my earlier patents a process has been described for the production of dyestuff images from diffusely dyed silver images. Thus, for example, according to my U. S. Patent No. 2,020,775, dated November 12, 1935, the production of such dyestuff images is performed by treating the diffusely dyed silver image with solutions which destroy the dye locally in the presence of the metal deposit of the photographic image. At the same time the silver is partially or totally converted into a silver compound. Individual cases, in which the destruction of the dye can be accelerated by the addition of certain substances, have been described in the above referred to patent.

It has been found that the effectiveness of the dye destroying solutions described in my U. S. Patent No. 2,020,775 and of the other dye destroying baths which were found to be applicable in the process, can be accelerated by a great number of substances other than those heretofore known. A large number of the substances added in accordance with this invention yield treating solutions which work in a much more effective manner, e. g. in much shorter time or in far smaller concentration, than the products previously proposed as accelerators. In view of the great effectiveness of the additions much smaller amounts of these accelerating substances are sufficient.

The present application is a division of my application Serial No. 179,591 filed December 13, 1937 (now Reissue Patent No. 22,308), wherein is claimed the use of reducible organic substances selected from the group of those reducible substances, the reduction products of which are reoxidizable during the treatment of a dyed silver image to the original reducible substance.

According to the present invention reducible organic dyes are used as accelerators in the process of producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and comprising a developed silver image. For converting the silver into a dye image a treating solution is used which contains a substance capable of selectively destroying said azo-dye by reduction in the presence of a metallic silver image and which further contains a small amount of the accelerating dye. The dye is of such a type as is reducible to form a reduction product which is reoxidizable under the conditions of the treating bath.

In order to illustrate the present invention several examples are set forth as follows:

Example 1

A photographic film carrying a silver halide emulsion layer is dyed with the dye Pontamine Sky Blue 6B (Schultz, Farbstofftabellen, 7th edition, 1931, vol. 1, No. 510) and an image is printed onto the film, developed and fixed. The film is treated with an 11% hydrochloric acid solution to which 0.2% auramine has been added. This treatment destroys the dye at the places of the metal deposit within a considerably shorter time than if the hydrochloric acid bath was used without the auramine. After the treatment with the dye-destroying bath the silver image is converted into a silver salt and fixed out.

Example 2

A photographic silver image uniformly dyed with Chlorantine Light Green BB (a dye furnished by the CIBA, Gesellschaft für Chemische Industrie, Basel, Switzerland) is treated with an 11% hydrochloric acid solution to which 0.2% sodium indigo sulfonate are added. This addition accelerates the destruction of the dye considerably.

Example 3

A silver image, as used in Examples 1 or 2, is treated with an 11% hydrochloric acid solution to which 0.2% of Alizarine Red S has been added. The addition renders the dye destruction more rapid.

Example 4

0.2% of N-ethyl-benzthiazol-carbocyanine iodide are used as an addition to the 11% hydrochloric acid solution and the solution is employed for treating silver images dyed with the dyes used in Examples 1 and 2.

Other examples of dye-destroying baths are described in my U. S. Patent No. 2,020,775 such, for example, as solutions of thiocarbamide and the parent application which matured into Patent 2,270,118 on January 13, 1942, and reissued as Patent Re. 22,308 dated May 11, 1943, discloses the use of dye-destroying baths comprising hydrobromic acid, sodium hyposulphite, 20% sodium chloride and hydrochloric acid, 20% magnesium chloride and hydrochloric acid in addition to a hydrochloric acid solution by itself. The dyes may be insoluble azo-dyes as well as azo-dyes that are soluble in water. In using insoluble azo-dyes which do not bleach readily with the dye-destroying solutions used alone, the difference in speed is more evident than if dyes are employed which are bleached out in shorter

times in a dye-destroying bath without admixture. Mention should, however, be made of the fact that the application of the admixtures has certain advantages even in the case of easily soluble and easily bleaching dyes, such as a shortening of the time of treatment and thereby a decrease of the detrimental effect on the layers.

The following dyes may be cited as further examples of accelerators: methyl violet B; alizarine-red-Agfa; dimethylaminostyryl dimethyl-thiazol-N-methyliodide; 6, methoxy-pseudocyanine N-ethyl-iodide; N-ethyl-6, methoxy-thiocarbocyanine-iodide; (3)-nitrostyryl-quinolinium-N-ethyl-ethylsulphonate; (3)-nitrostyryl-benzthiazol-ethyl-sulphonate; (3)-sulpho-styryl-pseudo-thiohydantoine; styryl-quinolinium-ethyl-sulphonate; (4)-dimethylamino-styryl-rhodanine. They may be used as additions to an 11% hydrochloric acid solution and used for the local destruction of the dyes referred to in the above examples. 0.2% of the dyes may be used.

The above examples are illustrative of methine and anthraquinone dyes which have been found effective as accelerators in dye destruction baths and in carrying on the process of the present invention. As will be seen, some of the above dyes are sensitizing dyes or desensitizing dyes. The accelerating effect appears to be in no direct proportion to the sensitizing properties but, on the contrary, to be based mainly on the fact that these dyes are substances which can be easily hydrated and which form reversible systems with their reduction products. The particular chemical structure, such as the presence of C=O or C=S groups in a carbocyclic or heterocyclic nucleus or in the quinone configuration may be responsible for the particular acceleration properties. Some of the dyes referred to above are typical examples of vat dyes and dyes capable of forming leuco compounds by reduction, which leuco compounds can be re-oxidized easily to the original dye.

What I claim is:

1. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a developed silver image, comprising hydrohalic acid and a small amount of an organic dye which is reducible and the reduction products of which are reoxidizable during the production of said dye image to the original reducible organic dye, the composition of said treating bath being such that the reduction products are reoxidizable during the production of said dye image and said treating bath being initially substantially free of reducing substances capable of being converted into said reducible substance by oxidation.

2. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a developed silver image, comprising hydrohalic acid and a small amount of a methine dye which is reducible during the production of the image.

3. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a developed silver image, comprising hydrohalic acid and a small amount of an anthraquinone dye which is reducible during the production of the image.

4. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed with an azo-dye and also comprising a developed silver image, comprising a substance capable of forming complex silver compounds and which acts to selectively destroy said azo-dye by reduction in the presence of said silver image and a small amount of an organic dye which is reducible and the reduction products of which are reoxidizable during the production of said image to the original reducible organic dye, the composition of said bath being such that the reduction products of said organic dye are reoxidizable during the production of said dye image and said bath being initially substantially free of reducing substances capable of being converted into said reducible dye by oxidation.

5. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed with an azo-dye and also comprising a developed silver image, comprising a substance capable of forming complex silver compounds and which acts to selectively destroy said azo-dye by reduction in the presence of said silver image and a small amount of an anthraquinone dye which is reducible during the production of said dye image.

6. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed with an azo-dye and also comprising a developed silver image, comprising a substance capable of forming complex silver compounds and which acts to selectively destroy said azo-dye by reduction in the presence of said silver image and a small amount of a methine dye which is reducible during the production of said dye image.

7. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed with an azo-dye and also comprising a developed silver image, comprising a substance capable of forming complex silver compounds and which acts to selectively destroy said azo-dye by reduction in the presence of said silver image and a small amount of a reducible vat dye which is reducible during the production of said dye image.

8. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed with an azo-dye and also comprising a developed silver image, comprising a substance capable of forming complex silver compounds and which acts to selectively destroy said azo-dye by reduction in the presence of said silver image and a small amount of a vat dye capable of forming a leuco-compound during the production of said dye image.

9. In the process of producing photographic dye images from silver images uniformly dyed by an azo-dye, the step of treating said silver images with a solution containing a substance capable of selectively destroying said azo-dye by reduction in the presence of a photographic silver image and comprising a small amount of an organic dye which is reducible and the reduction products of which are reoxidizable during the production of said dye images to the original organic dye, the composition of said solution being such that the reduction products of said organic dye are reoxidizable during the treatment of said silver images and said solution being substantially free of reducing substances capable of being converted into said reducible dye by oxidation.

10. In the process of producing photographic dye images from silver images uniformly dyed by an azo-dye, the step of treating said silver images with a solution containing a substance capable of selectively destroying said azo-dye by reduction in the presence of a photographic silver image

and comprising a small amount of a reducible methine dye.

11. In the process of producing photographic dye images from silver images uniformly dyed by an azo-dye, the step of treating said silver images with a solution containing a substance capable of selectively destroying said azo-dye by reduction in the presence of a photographic silver image and comprising a small amount of a reducible anthraquinone dye.

12. A process of producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and comprising a developed metal image, which consists in treating the said developed metal image with a solution containing an agent which is non-destructive with respect to the dye, but reacts with the said metal to oxidize it and substantially simultaneously to form a reducing substance which destroys said azo-dye at the points of the metal image, said solution further containing a small amount of an organic dye which is reducible and the reduction products of which are reoxidizable during the production of said image to the original reducible organic dye, the composition of said bath being such that the reduction products of said organic dye are reoxidizable during the production of said dye image and said bath being initially substantially free of reducing substances capable of being converted into said reducible dye by oxidation.

13. A process of producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and comprising a developed metal image, which consists in treating the said developed metal image with a solution containing an agent which is non-destructive with respect to the dye, but reacts with the said metal to oxidize it and substantially simultaneously to form a reducing substance which destroys said azo-dye at the points of the metal image, said solution further containing a small amount of a methine dye which is reducible during the production of said dye image.

14. A process of producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and comprising a developed metal image, which consists in treating the said developed metal image with a solution containing an agent which is non-destructive with respect to the dye, but reacts with the said metal to oxidize it and substantially simultaneously to form a reducing substance which destroys said azo-dye at the points of the metal image, said solution further containing a small amount of an anthraquinone dye which is reducible during the production of said dye image.

15. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a developed silver image, comprising hydrochloric acid and a small amount of an organic dye which is reducible and the reduction products of which are reoxidizable during the production of said image to the original reducible organic dye, the composition of said bath being such that the reduction products of said organic dye are reoxidizable during the production of said dye image and said bath being initially substantially free of reducing substances capable of being converted into said reducible dye by oxidation.

16. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a developed silver image, comprising hydrochloric acid and a small amount of a methine dye which is reducible during the production of the image.

17. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a developed silver image, comprising hydrochloric acid and a small amount of an anthraquinone dye which is reducible during the production of the image.

18. In the process of producing photographic dye images from silver images uniformly dyed by an azo-dye, the step of treating said silver images with a solution containing a substance capable of selectively destroying said azo-dye by reduction in the presence of a photographic silver image and comprising a small amount of a vat dye.

19. A process of producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a silver image, which comprises the step of treating said silver image with a solution comprising a substance which is capable of forming complex silver compounds and which acts to selectively destroy said azo-dye by reduction in the presence of said silver image and a small amount of a methine dye which is reducible during the production of said dye image.

20. A process of producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a silver image, which comprises the step of treating said silver image with a solution comprising a substance which is capable of forming complex silver compounds and which acts to selectively destroy said azo-dye by reduction in the presence of said silver image and a small amount of an anthraquinone dye which is reducible during the production of said dye image.

21. A process of producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a silver image, which comprises the step of treating said silver image with a solution comprising a substance which is capable of forming complex silver compounds and which acts to selectively destroy said azo-dye by reduction in the presence of said silver image and a small amount of a vat dye which is reducible during the production of said dye image.

22. A process of producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a silver image, which comprises the step of treating said silver image with a solution comprising a substance which is capable of forming complex silver compounds and which acts to selectively destroy said azo-dye by reduction in the presence of said silver image and a small amount of a reducible dye selected from the group consisting of anthraquinone, methine and vat dyes.

23. In the process of producing photographic dye images from silver images uniformly dyed by an azo-dye, the step of treating said silver images with a solution containing a substance capable of selectively destroying said azo-dye by reduction in the presence of a photographic silver image and comprising a small amount of a reducible dye selected from the group consisting of anthraquinone, methine and vat dyes.

24. A process of producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and comprising a developed metal image, which consists in treating the said developed metal image with a solution containing an agent which is non-destructive with respect to the dye, but reacts with the said metal to oxidize

it and substantially simultaneously to form a reducing substance which destroys said azo-dye at the points of the metal image, said solution further containing a small amount of a reducible dye selected from the group consisting of anthraquinone, methine and vat dyes.

25. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a developed silver image, comprising hydrohalic acid and a small amount of an organic dye selected from the group consisting of anthraquinone, methine and vat dyes.

26. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed with an azo-dye and also comprising a developed silver image, comprising a substance capable of forming complex silver compounds and which acts to selectively destroy said azo-dye by reduction in the presence of said silver image and a small amount of an organic dye selected from the group consisting of anthraquinone, methine and vat dyes.

27. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a silver image, comprising a substance which is non-destructive with respect to said azo-dye, but reacts with the silver to oxidize it and substantially simultaneously to form a reducing substance which destroys said azo-dye at the points of the silver image and also comprising a small amount of an anthraquinone dye which is reducible during the production of the dye image.

28. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a silver image, comprising a substance which is non-destructive with respect to said azo-dye, but reacts with the silver to oxidize it and substantially simultaneously to form a reducing substance which destroys said azo-dye at the points of the silver image and also comprising a small amount of a methine dye which is reducible during the production of the dye image.

29. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a silver image, comprising a substance which is non-destructive with respect to said azo-dye but reacts with the silver to oxidize it and substantially simultaneously to form a reducing substance which destroys said azo-dye at the points of the silver image and also comprising a small amount of a vat dye which is reducible during the production of the dye image.

30. A treating bath for producing a photographic dye image in a photographic emulsion uniformly dyed by an azo-dye and also comprising a silver image, comprising a substance which is non-destructive with respect to said azo-dye but reacts with the silver to oxidize it and substantially simultaneously to form a reducing substance which destroys said azo-dye at the points of the silver image and also comprising a small amount of an organic dye selected from the group consisting of anthraquinone, methine and vat dyes.

31. In a process of producing a dye image in a photographic emulsion comprising a metal image and an azo-dye, the step of treating said azo-dye in the presence of said metal image with an agent which in the presence of said metal image is capable of selectively destroying said azo-dye by reduction, said treatment being carried out in the presence of a quantity of a reducible organic dye sufficient to accelerate the selective destruction of said azo-dye, the said organic dye being selected from the group of those reducible organic dyes the reduction products of which are reoxidizable during said treatment of said azo-dye in the presence of said metal image to the original organic dye, said treatment with said reducible organic dye being initiated in the absence of reducing substances capable of being converted into said organic dye by oxidation and the conditions of said treatment being such that the reduction products of said organic dye are reoxidizable during said treatment of said azo-dye.

32. In a process of producing a dye image in a photographic emulsion comprising a silver image and an azo-dye, the step of treating said azo-dye in the presence of said silver image with an agent which in the presence of said silver image is capable of selectively destroying said azo-dye by reduction, said treatment being carried out in the presence of a quantity of a reducible organic dye sufficient to accelerate the selective destruction of said azo-dye, the said organic dye being selected from the group of those reducible organic dyes, the reduction products of which are reoxidizable during said treatment of said azo-dye in the presence of said silver image to the original organic dye, said treatment with said reducible organic dye being initiated in the absence of reducing substances capable of being converted into said organic dye by oxidation and the conditions of said treatment being such that the reduction products of said organic dye are reoxidizable during said treatment of said azo-dye.

33. In a process of producing a dye image in a photographic emulsion comprising a silver image and an azo-dye, the step of treating said azo-dye in the presence of said silver image with an agent which in the presence of said silver image is non-destructive with respect to the dyestuff, but reacts with the said silver to oxidize it and substantially simultaneously to form a reducing substance which destroys said azo-dye at the points of the silver image, said treatment being carried out in the presence of a quantity of a reducible organic dye sufficient to accelerate the selective destruction of said azo-dye, the said organic dye being selected from the group of those reducible organic dyes, the reduction products of which are reoxidizable during said treatment of said azo-dye in the presence of said silver image to the original organic dye, said treatment being initiated with said reducible organic dye in the absence of reducing substances capable of being converted into said organic dyes by oxidation and the conditions of said treatment being such that the reduction products of said organic dye are reoxidizable during said treatment of said azo-dye.

34. In a process of producing a dye image in a photographic emulsion comprising a silver image and an azo-dye, the step of treating said azo-dye in the presence of said silver image with a solution comprising hydrohalic acid, said treatment being carried out in the presence of a quantity of a reducible organic dye sufficient to accelerate the selective destruction of said azo-dye, the said organic dye being selected from the group of those organic dyes, the reduction products of which are reoxidizable during said treatment of said azo-dye in the presence of said silver image to the original organic dye, said treatment with said reducible organic dye being initiated in the absence

of reducing substances capable of being converted into said reducible organic dye by oxidation and the conditions of said treatment being such that the reduction products of said reducible organic dye are reoxidizable during said treatment of said azo-dye.

35. In a process of producing a dye image in a photographic emulsion comprising a silver image and an azo-dye, the step of treating said azo-dye in the presence of said silver image with a solution comprising hydrochloric acid, said treatment being carried out in the presence of a quantity of a reducible organic dye sufficient to accelerate the selective destruction of said azo-dye, the said organic dye being selected from the group of those organic dyes, the reduction products of which are reoxidizable during said treatment of said azo-dye in the presence of said silver image to the original organic dye, said treatment with said reducible organic dye being initiated in the absence of reducing substances capable of being converted into said reducible organic dye by oxidation and the conditions of said treatment being such that the reduction products of said organic dye are reoxidizable during said treatment of said azo-dye.

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