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PHOTOGRAPHIC PRODUCTS, PROCESSES,
AND COMPOSITIONS

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The present invention is concerned with photography and more particularly with photographic products and processes for producing photographic images having increased density.

One object of this invention is to provide processes for producing photographic images having increased density.

Another object of this invention is to provide novel photographic products embodying the means for increasing the density of a photographic image.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description.

When a photographic emulsion is exposed to light, or other form of radiant energy, the grains of silver halide in the exposed areas are rendered developable and, upon development, are reduced to metallic silver. The density of the resulting images, in general, is dependent upon the number of grains of silver produced, the size of the grains, and the interspatial distance between said grains.

I have discovered that photographic images, having increased density, may be produced by carrying out the development in the presence of a polymerizable vinyl monomer and causing said monomer to be polymerized during the development step. Apparently, the polymer, produced, serves to bind the exposed and developed crystals which thereby exhibit a very dense image since light scattering per unit weight of developed silver is considerably decreased on aggregation of the grains.

In carrying out the processes of this invention a latent silver halide image is developed with a developing agent which, upon oxidation, passes through a free radical state. The free radicals, produced as intermediate oxidation products of the developing agent during the development, are used to initiate and propagate the polymerization of the vinyl monomer. The areas of polymerization will be substantially coextensive with the areas in which reduction of silver halide and oxidation of the developing agent are taking place (i.e., the exposed areas) and little, if any, polymer will be produced in unexposed areas. A group of developers, which pass through a free radical state upon being oxidized and which are especially useful in carrying out the processes of this invention, are those of the benzenoid class. In general, developing agents of this class contain an aryl nucleus substituted in the ortho and para positions, with respect to each other, by hydroxyl and/or amino groups, including alkyl and aryl substituted amino groups. The aryl nucleus in such developers may also be further substituted by other substituents such, for example, as alkyl, aryl, alkoxy, etc., groups. As examples of benzenoid developing agents which are useful in carrying out the processes of this invention, mention may be made of p-aminophenol hydrochloride, 2-amino-5-diethylaminotoluene hydrochloride, p-toluidine, p-methylaminophenol sulfate, hydroquinone diacetic acid, 3,5-dimethyl-

yl-4-aminophenol, p-benzylaminophenol, 2,6-dimethyl-4-aminophenol, 4-amino-1-naphthol hydrochloride, 2,5-dimethyl-4-aminophenol, 4-anilinophenol, 4-amino-2-methoxy-phenol and p-phenylene diamine.

Since the life cycle of the free radicals, produced during development, is generally of short duration, the vinyl monomer must be present at the time of development. It has been found that no increase in density or polymerization will occur if the monomer is added after development. In a preferred mode of carrying out the processes of this invention, the vinyl monomer is incorporated in the photosensitive emulsion prior to exposure. This may be readily accomplished, for example, by dissolving or emulsifying the monomer in the silver halide emulsion coating solution prior to its application to a suitable support. In certain instances the developing agent may be incorporated along with the vinyl monomer into the photosensitive element prior to exposure. In such an embodiment the developing agent may be rendered operative after exposure by permeating the photosensitive element with an aqueous alkaline solution. In another useful mode of carrying out the invention, the monomer is incorporated in the developing solution and imbibed on the photosensitive emulsion along with the developing agent.

Monomers suitable for use in the processes herein disclosed may be selected from any of the polymerizable vinyl monomers available. It will be understood that the especially useful monomers are those which are readily dissolved or emulsified in the photosensitive emulsion or developing solution. A preferred class of monomers are the salts of vinyl acids. Such monomers have low vapor pressures, and thus the photosensitive elements in which they are incorporated will have considerably longer shelf lives. The amount of vinyl monomer incorporated will depend upon the amount of intensification desired. Photosensitive emulsions wherein the monomer constitutes about 20% of the carrier material (for example, gelatin) have been found to be especially useful. As examples of vinyl monomers contemplated to be useful in the processes herein disclosed, mention may be made of calcium acrylate, sodium acrylate, sodium methacrylate, alkyl methacrylates, alkyl acrylates, vinylacetate, cinnamaldehyde, cinnamic acid, cinnamic alcohol, acrolein, acrylonitrile, styrene, etc. It should be understood that the term "vinyl monomer" is intended to include divinyl monomers such, for example, as divinylbenzene, glycol diacrylates, etc., which will produce a crosslinked polymer. It should be further understood that more than one monomer may be used, and thus a copolymer will be produced upon polymerization.

The developing step is carried out under conditions which promote the production of free radicals with a sufficient lifespan to initiate polymerization, such as the conditions conducive to color coupling. Excessively high pH's which are generally detrimental to the stability of most free radicals should be avoided.

The following nonlimiting examples illustrate the processes of this invention.

Example 1

A suspension of silver bromide crystals (average size about one micron) was made up in water using a trace of glue as the stabilizer. The suspension was exposed to blue light and divided into two parts. One part was developed with a 1/10 N p-aminophenol hydrochloride solution buffered at pH 8 and the other was developed with another portion of the same solution to which was added 20%, by weight, of calcium acrylate. After about fifteen minutes the sample which contained monomer turned an intense black and a large precipitate finally settled out. The sample without monomer turned into a murky brown stable suspension.

Example 2

Two silver bromide gelatin emulsion plates were made up and exposed to feeble light. One plate was developed by conventional means with p-aminophenol and a barely perceptible image was obtained. The other element was developed with p-aminophenol in the presence of calcium acrylate, with a short warming at 35° C., and an intense black-and-white image was obtained.

In addition to conventional photographic processes, such as described above, the processes of this invention are equally useful in silver transfer processes such, for example, as those disclosed in U.S. Patent No. 2,662,822. In such processes a sheet of photosensitive material, preferably a silver halide, is exposed to actinic light to create therein a latent negative image. This latent image is developed and a positive image thereof is formed on a superposed image-receiving layer, preferably by creating between the superposed layers a uniform film of a viscous alkaline developer solution containing a substance capable of forming positive image-forming components. This latter substance, in a preferred form of the invention, comprises a silver halide solvent such as sodium thiosulfate. With such a film of liquid composition between the exposed photosensitive layer and the image-receiving layer, the developer therein develops the exposed photosensitive material and the silver halide solvent forms soluble complex ions with the unexposed photosensitive material. These complex ions are transferred and imbibed on the image-carrying layer (which may contain silver precipitating agents) where they are reacted to form a positive image of the latent negative image.

In silver transfer processes, such as described above, the processes of the present invention may be used to prevent staining in the highlights of the transferred positive image. This object may be accomplished by having polymerizable vinyl monomers present during the development of the latent negative image and using the resulting polymer to at least assist in preventing the transfer of undeveloped silver halide from such areas. The vinyl monomer may be incorporated in the photosensitive element or in the developer solution.

The processes of this invention may also be used in silver transfer processes to intensify the transferred positive image. This intensification may be accomplished by carrying out the reduction of the transferred silver ions in the presence of a polymerizable vinyl monomer. The vinyl monomer may be disposed in the image-receiving element prior to processing, or it may be imbibed from the processing solution. When a vinyl monomer is used in the photosensitive emulsion and said monomer is soluble in the liquid processing solution, unreacted monomer from said photosensitive element may be transferred to the image-receiving element and used to intensify the positive image. The resulting increased density is apparently attributable, as in conventional photography, to the aggregating effect of the polymer produced.

The processes of the present invention are further useful in color diffusion transfer processes. They are especially useful in processes wherein a complete dye, soluble in aqueous alkaline solutions, is incorporated in or behind a silver halide emulsion and its transfer to a superposed image-receiving element is controlled by reducing the permeability of the emulsion in exposed areas. The processes of the present invention enable one to control the transfer of the dye by creating in the exposed areas polymeric barriers having reduced permeability to the dye. These barriers may be created by carrying out the development of the latent image in the presence of a suitable vinyl monomer.

The processes of this invention are still further useful in the preparation of relief images. Such images may be made, for example, by developing a silver halide gelatin emulsion in the presence of a suitable polymerizable vinyl monomer and, after development, washing the resulting image with a material which is a solvent for the emulsion

and the monomer, but not for the resulting polymer. In certain instances, the relief images may be used as printing plates in conventional mechanical printing processes.

Colored polymeric images can be produced by the processes of this invention by using a primary aromatic amino silver halide developer (i.e., a color developer) as the developing agent and carrying out the development in the presence of a color coupler in addition to the vinyl monomer. Thus, for example, a red polymeric image is produced by developing exposed silver halide with a solution comprising equimolar amounts of p-aminophenol hydrochloride and 1-(2'-chloro-5'-sulfophenyl)-3-methyl-5-pyrazolone coupler and 20%, by weight, of calcium acrylate, buffered at pH 8.

Since certain changes may be made in the above product and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic process comprising the steps of permeating a photosensitive element including an exposed silver halide emulsion layer with a free radical polymerizable vinyl monomer, developing the exposed silver halide emulsion with a benzenoid silver halide developer, which developer forms free radicals upon being oxidized as a function of development and polymerizing said polymerizable vinyl monomer with said free radicals in the exposed and developed areas.

2. A photographic process as defined in claim 1 wherein said benzenoid silver halide developer is p-aminophenol.

3. A photographic process as defined in claim 1 wherein said polymerizable vinyl monomer is calcium acrylate.

4. A process as defined in claim 1 wherein said silver halide developer and said polymerizable vinyl monomer are applied to the photosensitive element from the same processing solution.

5. A photographic process comprising the steps of developing a photosensitive element including an exposed silver halide emulsion in the presence of a free radical polymerizable vinyl monomer which is in the emulsion at the time of development, with a benzenoid silver halide developer, which developer forms free radicals upon being oxidized as a function of development, polymerizing said vinyl monomer with said free radicals in the exposed and developed areas and subsequent to development washing said photosensitive element with a solvent in which the emulsion is soluble and the resulting polymer is insoluble to produce a relief image.

6. A photographic process comprising the steps of developing a photosensitive element, including an exposed silver halide emulsion layer, which has therein at the time of development a free radical polymerizable vinyl monomer, a silver halide solvent and a benzenoid silver halide developer, which developer forms free radicals upon being oxidized as a function of development, polymerizing said vinyl monomer with said free radicals in exposed and developed areas, forming a soluble complex between said silver halide solvent and undeveloped silver halide and transferring said complex to a superposed image-receiving element to produce a transfer image on said image-receiving element.

7. A photographic process as defined in claim 6 wherein said polymerizable vinyl monomer is soluble in an aqueous alkaline processing solution.

8. In a photographic process comprising the steps of developing a photosensitive element including an exposed silver halide emulsion layer with a benzenoid silver halide developer, which developer forms free radicals upon being oxidized as a function of development, and a silver halide solvent, and superposing said photosensitive element on an image-receiving element to produce a transfer image on said image-receiving element, the improvement of having a free radical polymerizable vinyl monomer in

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the image-receiving element and polymerizing said vinyl monomer with said free radicals in the developed areas of said image-receiving element.

9. A photographic process as defined in claim 1 wherein said silver halide developer is a primary aromatic amino silver halide developer and the development of said exposed silver halide emulsion is carried out in the presence of a color coupler in addition to said polymerizable vinyl monomer to produce a colored polymeric image, 10

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said coupler being in the silver halide emulsion at the time of development.

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