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3,291,608

# ENHANCED ACTIVITY OF NUCLEI FOR PHYSICAL DEVELOPMENT

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This invention relates to physical development nuclei of enhanced activity and the use of these nuclei in preparing photographic products.

There are two basic methods for obtaining developed silver images, one of which is chemical or direct development and the second method is termed physical development. By the latter method a physical developer is used containing a reducing agent, a soluble silver salt as a source of free silver ions, and other materials to adjust pH and silver ion concentration. These solutions deposit silver upon nuclei which may be zinc sulfide, lead sulfide, nickel sulfide, silver selenide, colloidal gold, colloidal silver or the like. In a modified form of physical development referred to as prefixation physical development the silver halide is not dissolved out first but the developer solution contains a strong silver halide solvent such as sodium thiosulfate which dissolves the halide as development proceeds.

One object of my invention is to provide nuclei having enhanced activity in physical development operations. Another object of my invention is to provide a method of making zinc sulfides which are especially adapted for use in products intended for physical development. A further object of my invention is to provide photographic products intended for physical development in which sulfides of enhanced activity in accordance with the invention are employed. Other objects of my invention will appear herein.

I have found that metallic physical development nuclei prepared in the presence of a chloranil-modified gelatin exhibit superior properties when employed in physical development operations. The gelatin employed as the peptizing material in preparing these nuclei is formed by adding tetrachloro-p-benzoquinone (chloranil) to an aqueous solution of gelatin whereupon modification of the gelatin occurs. The thus modified gelatin is then employed as the peptizing material for various metallic physical development nuclei.

The preparation of chloranil-modified gelatin may conveniently be carried out as follows: 250 grams of a 10% aqueous solution of bone gelatin was dissolved in 650 cc. of distilled water at 40° C. 5 grams of tetrachloro-p-benzoquinone was added to the gelatin solution and the mass was stirred for 4 hours at room temperature. The mass was filtered thereby giving a turbid solution which was subjected to centrifuging. There was thus obtained a clear red gelatin solution which was decanted from the yellow residue present and the mass was made up with distilled water to a total volume of 900 cc.

For nuclei in physical development operations metallic nuclei have been suggested, some of which are more useful for this purpose than others. The following description of preparing zinc sulfide may be followed in the making of other metallic physical development nuclei useful in photographic products. The solution of chloranil-modified gelatin obtained as described above at 40° C. was mixed with a solution of 1.26 grams anhydrous sodium sulfite in 74 cc. distilled water and then with 2.65 cc. of 0.944 Normal  $\text{Na}_2\text{S}$ . Immediately after mixing in the sodium sulfide a solution of 2.60 cc. of 0.99 Normal zinc nitrate in 270 cc. of distilled water was run into the mass while stirring over a period of 4 minutes, 35 seconds. There was thus formed a sol of zinc sulfide

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in gelatin which mass was then chill set, noodled and washed with cold water to remove the water soluble salts therefrom. The material thus prepared was coated out onto a support such as cellulose triacetate or polyethylene terephthalate at a coverage of 0.296 gram of gelatin and 0.00144 gram of zinc sulfide per square foot. The coating was developed at 25° C. in a direct physical developer having the following composition:

## 4-amino-3-methyl-N-ethyl-N(beta-hydroxyethyl)aniline

|    |                                                                   |         |                     |
|----|-------------------------------------------------------------------|---------|---------------------|
| 10 | $\frac{1}{2}\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ----- | grams-- | 1.274               |
|    | $\text{K}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ -----            | do----  | 50.0                |
|    | $[\text{Ag}^+]^1$ -----                                           | moles-- | $1 \times 10^{-12}$ |
|    | Distilled water to make 1000 cc.                                  |         |                     |

15 The pH was adjusted to 12.0 with 6 N  $\text{H}_2\text{SO}_4$ .

<sup>1</sup> The free silver ion concentration was adjusted from a solution of  $\text{Ag}(\text{S}_2\text{O}_3)_2^{2-}$  prepared from  $\text{AgCl}$  and  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ . The total silver ion concentration of the developer was  $5 \times 10^{-3}$  moles/l.

20 It was found that by the use of zinc sulfide nuclei prepared in chloranil-modified gelatin more active centers for physical development result than in the case of like products in which the zinc sulfide is prepared in an untreated gelatin.

25 The following example illustrates the use of colloidal zinc sulfide nuclei prepared in accordance with the invention in photographic products including a silver halide photographic emulsion. A photographic product was obtained composed of a cellulose acetate support having thereon a layer of silver bromiodide photographic emulsion coated at a coverage of 100 mg. of silver and 230 mg. of gelatin per square foot, over which was applied a layer of colloidal zinc sulfide nuclei prepared in accordance with the invention which layer contained 0.2 mg. of zinc sulfide and 560 mg. of gelatin per square foot. The described product was exposed in an Eastman 1B sensitometer for 1/100 of a second. It was developed in a developer having the following composition:

|    |                                          |         |      |
|----|------------------------------------------|---------|------|
| 40 | Water about 125° F. (50° C.) -----       | cc--    | 500  |
|    | N-methyl-p-aminophenol sulfate (Elon) -- | grams-- | 3.1  |
|    | Sodium sulfite, desiccated -----         | do----  | 45.0 |
|    | Hydroquinone -----                       | do----  | 12.0 |
|    | Sodium carbonate, desiccated -----       | do----  | 67.5 |
|    | Potassium bromide -----                  | do----  | 1.9  |
| 45 | Sodium thiosulfate -----                 | do----  | 4    |
|    | Water to make 1.0 liter.                 |         |      |

50 The product was subsequently rinsed, fixed for 2 minutes in a hypo fixing bath, washed and dried. It was found that a low contrast negative image was obtained in the exposed areas and a positive image was obtained in the unexposed areas which had considerably greater density than that produced by the use of zinc sulfide nuclei prepared in untreated gelatin. Greater differentiation was therefore obtained between the contiguous negative and positive images when nuclei dispersed in the chloranil-modified gelatin were utilized.

55 In other cases zinc sulfide nuclei were incorporated directly in silver halide emulsion layers rather than in a separate layer. In those cases the zinc sulfide prepared in chloranil-modified gelatin produced higher density positive images in the unexposed areas than were untreated gelatin was employed. This is also true in products adapted for use in silver halide diffusion transfer processes such as in the type described in U.S. Patent No. 3,020,155 in that more active physical development was observed than is found where untreated gelatin is employed.

70 The invention although illustrated in connection with zinc sulfide nuclei is not restricted thereto. Other physical development nuclei such as colloidal gold of silver, metallic sulfides, selenides or tellurides such as lead sulfide, nickel sulfide, colloidal silver selenide, colloidal silver

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telluride, or other metallic physical development nuclei mentioned in the prior art as useful for this purpose can be prepared and used either as the sole development nuclei or mixed with one another in accordance with the invention.

The colloidal metals may be prepared in the presence of a chloranil-modified gelatin by the dextrin reduction method of preparation of Carey-Lea as described in "Colloidal Elements," by Weiser, John Wiley and Sons, New York, New York, 1933, page 119. Metallic as used herein refers to heavy metals and their salts such as are useful as physical development nuclei.

The invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

I claim:

1. A composition useful in preparing photographic products which comprises chloranil-modified gelatin containing, dispersed therein, metallic physical development nuclei formed in situ.

2. A composition useful in preparing photographic products which comprises chloranil-modified gelatin containing, dispersed therein, zinc sulfide physical development nuclei formed in situ.

3. A composition useful in preparing photographic products which comprises chloranil-modified gelatin containing, dispersed therein, colloidal silver physical development nuclei formed in situ.

4. A method of preparing metallic physical development nuclei which comprises preparing a dispersion in finely divided form resulting from introducing an aqueous solution of zinc salt and an aqueous solution of a water-soluble sulfide into an aqueous solution of chloranil-modified gelatin.

5. A product useful in reproduction procedures comprising a support having thereon a layer containing a dispersion of metallic physical development nuclei in chloranil-modified gelatin and wherein said dispersion is obtained by preparing the metallic physical development nuclei in the chloranil-modified gelatin.

6. A product useful in reproduction procedures comprising a support having thereon a layer containing a dispersion of zinc sulfide physical development nuclei in chloranil-modified gelatin and wherein said dispersion is

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obtained by preparing zinc sulfide in the chloranil-modified gelatin.

7. A product useful in reproduction procedures comprising a cellulose acetate support having thereon a layer containing a dispersion of zinc sulfide physical development nuclei in chloranil-modified gelatin and wherein said dispersion is obtained by preparing zinc sulfide in the chloranil-modified gelatin.

8. A photographic material comprising a support having thereon a layer of a silver halide photographic emulsion and a layer containing metallic physical development nuclei formed in situ in chloranil-modified gelatin.

9. A photographic material comprising a support having thereon a layer of a silver halide photographic emulsion and a layer containing zinc sulfide physical development nuclei in chloranil-modified gelatin and wherein said zinc sulfide physical development nuclei are obtained by preparing zinc sulfide in the chloranil-modified gelatin.

10. A photographic development process wherein a photographic material comprising a support having thereon a layer of a silver halide photographic emulsion and a layer containing metallic physical development nuclei formed in situ in chloranil-modified gelatin is exposed and developed by a physical photographic developer.

11. A photographic development process wherein a photographic material comprising a support having thereon a layer of a silver halide photographic emulsion and a layer containing zinc sulfide physical development nuclei in chloranil-modified gelatin and wherein said zinc sulfide physical development nuclei are obtained by preparing zinc sulfide in the chloranil-modified gelatin is exposed and developed by a physical photographic developer.

#### References Cited by the Examiner

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