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3,189,453
PHOTOGRAPHIC EMULSIONS CONTAINING THIO DERIVATIVES AS FIXERS AND METHOD OF USING SAME

Arthur H. Herz and Norman W. Kalenda, both of Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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13 Claims. (Cl. 96—61)

This invention relates to photographic compositions. Preferred embodiments of the invention concern photographic silver halide emulsions containing certain addenda that can serve as stabilizing agents obivating the necessity of conventional fixing.

After a photographic silver halide emulsion is developed and a silver image is produced in the areas of exposure, the silver halide in the unexposed areas is conventionally washed out as a soluble complex with a fixing solution. It would be convenient to have the fixing agent incorporated directly in the emulsion. However, usual fixing agents are not suitable for incorporation directly in emulsions as they form complexes with silver halide regardless of the acidity of the environment and they would destroy the photographic properties of the emulsion during its manufacture. Also many fixing agents would cause substantial desensitization of the emulsion if incorporated therein. It is thus desirable to have fixing materials that are sufficiently compatible with photographic silver halide emulsions so that they can be utilized therein.

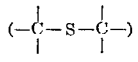
It is an object of this invention to provide a new class of photographic emulsion fixing addenda.

It is another object of this invention to provide novel photographic silver emulsions that are fixed on development in an aqueous alkaline solution.

It is still another object of this invention to provide a new method for processing photographic silver halide emulsions without a separate fixing step.

It is likewise an object of this invention to provide a novel photographic element that can be substantially concomitantly developed and fixed.

These and other objects of the invention are accomplished in accordance with the invention with photographic silver halide emulsions having incorporated therein a thioether compound having a sulfur atom attached to two carbon atoms



and which thioether has substantial stability in photographic silver halide emulsion at pH's of 7 or less and liberates a compound having a thiol radical (—SH) capable of forming a substantially light stable complex with silver halide under aqueous conditions at pH's greater than 7. Illustrative thioether addenda of the invention have attached to an alpha carbon atom, with reference to the sulfur atom, a radical containing a second sulfur atom, a nitrogen atom or an oxygen atom. Other thioether addenda of the invention have attached to a beta carbon atom, with reference to the sulfur atom, an electron-withdrawing group or an unsaturated group, such as an amide radical, a keto radical, a nitrile radical, a sulfonyl radical, a carboxyl radical and the like.

An especially useful class of thioether compounds of the invention are thiazoline derivatives including ortho

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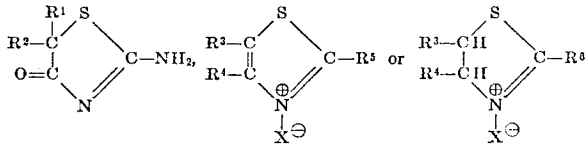
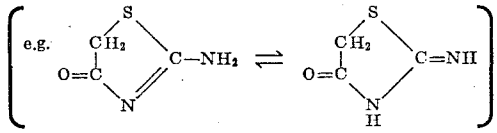
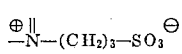
and meta thiazoles and thiazolines. Typical suitable thiazoline derivatives have the formula



Certain of such derivatives have corresponding tautomeric forms, such tautomeric forms being included in our invention

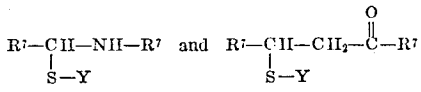


In the above formulas, R^1, R^2, R^5 and R^6 can be either hydrogen atoms or hydrocarbon radicals such as alkyl radicals or aryl radicals, typical suitable alkyl radicals having 1 to 20 carbon atoms and generally 1 to 8 carbon atoms such as methyl, n-propyl, 2-ethylhexyl, n-decyl, stearyl, n-eicosyl, etc., and typical suitable aryl radicals being phenyl and alkyl-substituted phenyl radical. In the above formulas, R^3 and R^4 can be hydrogen atoms, hydrocarbon radicals as described above for R^1, R^2, R^5 and R^6, hydrocarbon radicals containing such substituents as hydroxyl radicals, or R^3 and R^4 together can be the necessary carbon and hydrogen atoms to form an aryl radical which includes the adjacent carbon atoms on the thiazoline nucleus. In the above formulas, X, in combination with the adjacent nitrogen atom on the thiazoline nucleus forms a covalent quaternary salt having no hydrogen atom attached to the nitrogen atom. The quaternary salt can include an electro-negative group such as sulfonate, carboxylic acid groups or the like to form an inner salt such as is illustrated by the quaternary salt group



or alkyl quaternary salts including an anion or negatively charged ion such as a chloride ion, a perchlorate ion, a p-toluenesulfonate ion or the like such as illustrated by the quaternary salt group

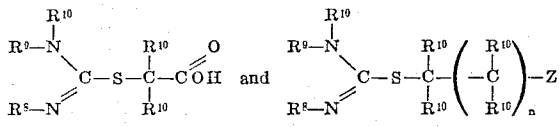
Another useful class of thioether addenda are described in detail in our application titled "Photographic Silver Halide Emulsions Containing Thioether Derivatives," U.S. Serial No. 133,768, which was filed concurrently herewith, now U.S. Patent No. 3,140,178. Typical thioether addenda of this copending application have the formulas



wherein R^7 is an aryl radical and Y is an organic radical such as an aryl radical, an aralkyl radical, a substituted alkyl radical, an alkyl radical, a heterocyclic radical or the like.

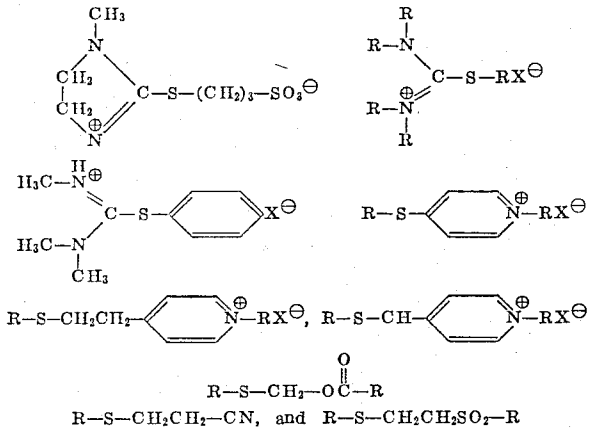
Still another useful class of thioether addenda are described in detail in our application titled "Photographic

Silver Halide Emulsions Containing Isothiourea Derivatives," U.S. Serial No. 133,769, which was also filed concurrently herewith. Typical thioether addenda of this copending application have the formulas



wherein R^8, R^9 and R^{10} can be hydrogen atoms or hydrocarbon radicals. R^8 and R^9 can also be acyl radicals or the necessary carbon and hydrogen atoms to form an alkylene radical linking both adjacent nitrogen atoms to form a cyclic nucleus. The letter *n* can be an integer of 1 to 10. The letter Z can be a carboxyl radical, a sulfonate radical, a hydroxyl radical or an amino radical, Z being other than a carboxyl radical when *n* is 1 and R^{10} is H.

Other related thioether addenda of the invention include compounds having the structural formulas:



wherein X is an anion and wherein R is an organic radical including such hydrocarbons as alkyl or aryl, and heterocyclic radicals, which can be substituted with hydroxyl, carbonyl, amino, sulfonyl and the like radicals. Likewise, such thioethers as thiomethyl esters as illustrated by β-morpholino-ethylthiomethyl acetate hydrochloride are included in our invention.

The photographic silver halide emulsion addenda of the invention serve as incorporated fixing or image stabilizing agents. These addenda do not prevent development of exposed areas of the emulsion but protect the unexposed areas against print out after development of the emulsion. Thus with emulsions containing the addenda of the invention silver images can be formed and stabilized without the use of a conventional fixing process. The subject addenda are stable and do not act as fixing agents in acidic or neutral media. However, under aqueous alkaline conditions, such as conventionally prevail during the developing of photographic emulsions, the subject addenda are active fixing agents. Generally alkaline developing pH's of 9 or higher are utilized for rapid fixing. Under alkaline conditions the subject thioethers liberate a thiol compound which reacts with the unexposed and undeveloped silver halide of the emulsion forming a product which is more stable than silver halide to light, atmosphere and reducing conditions, and which complex does not decompose to silver or silver sulfide. The subject addenda are used in photographic silver halide emulsions and utilized at a concentration of at least one mole of the addendum per mole of silver halide in the emulsion.

The preparation of photographic silver halide emulsions such as are used with the addenda of the invention involves three separate operations: (1) emulsification and digestion of silver halide, (2) the freeing of the emulsion of excess water-soluble salts, suitably by washing with water, and (3) the second digestion or "after-ripening" to obtain increased emulsion speed or sensitivity. (Mees, "The Theory of the Photographic Process," 1954.) The addenda of the invention can be added to the emulsion before the final digestion or after-ripening, or they can be added immediately prior to the coating.

The addenda of the invention can be added to photographic emulsions using any of the well-known techniques in emulsion making. For example, they can be dissolved in a suitable solvent and added to the silver halide emulsion, or they can be added to the emulsion in the form of a dispersion similar to the technique used to incorporate certain types of color forming compounds (couplers) in a photographic emulsion. Techniques of this type are described in Jelley et al. U.S. Patent 2,322,027, issued June 15, 1943, and Fierke et al. U.S. Patent 2,801,171, issued July 30, 1957. The solvent should be selected so that it has no harmful effect upon the emulsion in accordance with usual practice, and generally solvents or diluents which are miscible with water are to be preferred. Water alone is a dispersing medium for some of the sensitizers of the invention. In other cases, the subject sensitizers can be dissolved in solvents, such as ethanol, acetone, pyridine, N,N-dimethylformamide, etc., and added to the emulsion in this form.

The emulsions of the invention can include the usual photographic addenda such as chemical sensitizers, optical sensitizers, stabilizers or antifoggants, plasticizers, hardeners, coating aids, and the like.

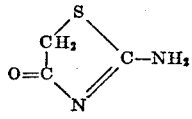
Various silver salts can be used as the sensitive salt such as silver bromide, silver iodide, silver chloride, or mixed silver halides such as silver chlorobromide or silver bromoiodide.

In the preparation of the silver halide dispersions employed for preparing silver halide emulsions, there can be employed as the dispersing agent for the silver halide in its preparation, gelatin or some other colloidal material such as colloidal albumin, a cellulose derivative, or a synthetic resin, for instance, a polyvinyl compound, although gelatin is preferred. Some colloids which can be used are polyvinyl alcohol or a hydrolyzed polyvinyl acetate as described in Lowe U.S. Patent 2,286,215, issued June 16, 1942; a far hydrolyzed cellulose ester such as cellulose acetate hydrolyzed to an acetyl content of 19–26% as described in U.S. Patent 2,327,808 of Lowe and Clark, issued August 24, 1943; a water-soluble ethanolamine cellulose acetate as described in Yutzy U.S. Patent 2,322,085, issued June 15, 1943; a polyacrylamide having a combined acrylamide content of 30–60% and a specific viscosity of 0.25–1.5 of an imidized polyacrylamide of like acrylamide content and viscosity as described in Lowe, Minsk and Kenyon U.S. Patent 2,541,474, issued February 13, 1951; zein as described in Lowe U.S. Patent 2,563,791, issued August 7, 1951; a vinyl alcohol polymer containing urethane carboxylic acid groups of the type described in Unruh and Smith U.S. Patent 2,768,-154, issued October 23, 1956; or containing cyano-acetyl groups such as the vinyl alcohol-vinyl cyanoacetate copolymer as described in Unruh, Smith and Priest U.S. Patent 2,808,331, issued October 1, 1957; or a polymeric material which results from polymerizing a protein or a saturated acylated protein with a monomer having a vinyl group as described in Illingsworth, Dann and Gates U.S. Patent 2,852,382, issued September 19, 1958. If desired, compatible mixtures of two or more of these colloids can be employed for dispersing the silver halide in its preparation.

The above-described emulsions of the invention can be coated on a wide variety of supports in accordance with usual practice. Typical supports for photographic elements of the invention include cellulose nitrate film, cellulose acetate film, polyvinyl acetal film, polystyrene film, polyethyleneterephthalate film and related films of resinous materials, as well as glass, paper, wood, metals and others.

Illustrative emulsion addenda of the invention have the following structural formulas:

COMPOUND 1



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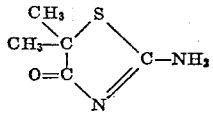

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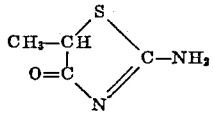

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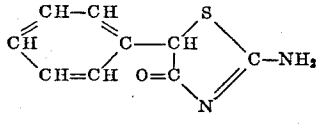

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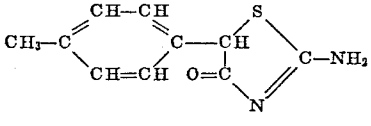

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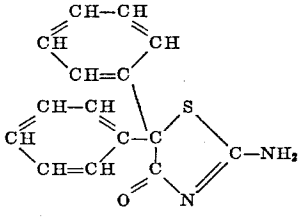

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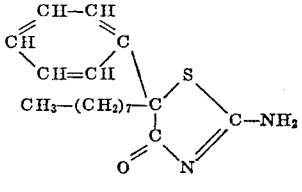

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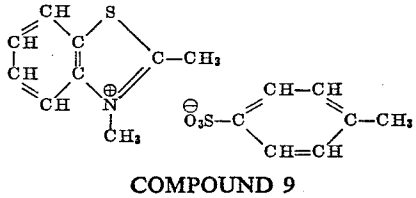

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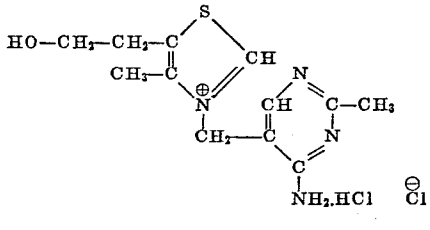

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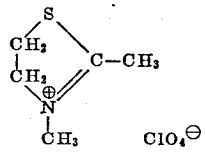

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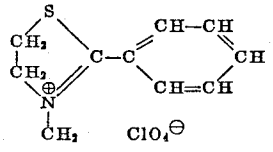

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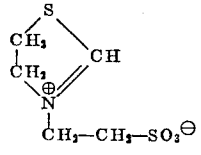

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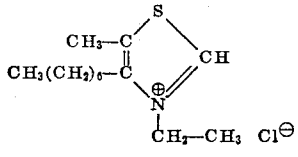

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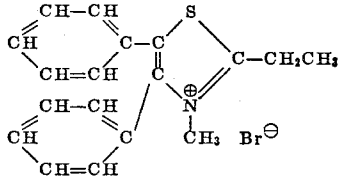

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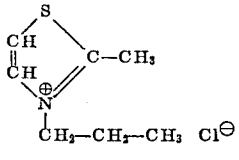

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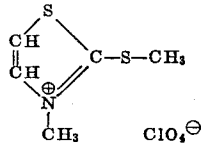

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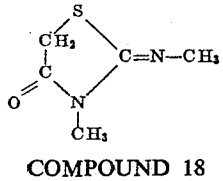

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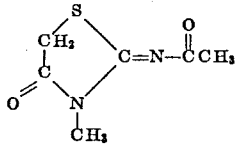

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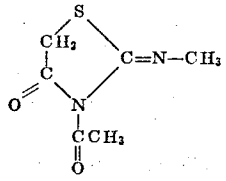

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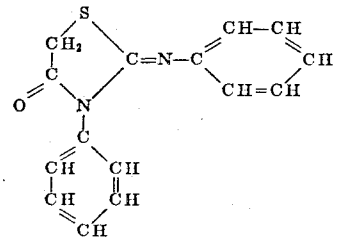


The invention is illustrated by the following examples wherein representative members of the above-described compounds were utilized as incorporated fixers in photographic silver halide emulsions.

Example 1

To a photographic gelatino-silver bromide emulsion containing .05 mole of silver bromide per 400 cc. of 6.25% aqueous gelatain solution was added Compound 1 described above in an amount equal to about 2 moles thereof per mole of silver bromide which was then coated on a cellulose acetate film support at an amount of 10 cc. of emulsion per 5 inch by 14 inch area of support. The resulting film was then exposed through a negative for 10 seconds at 34 inches with a 60 watt light bulb. The film was then developed for 10 minutes at 68° F. in a developer having the formula:

	G.
Sodium sulfite (anhydrous)	90
Hydroquinone	45
Sodium hydroxide	37
Potassium bromide	30
Water to make one liter.	

After a 2 second water rinse the resulting film was permitted to dry under ordinary room illumination without further processing. The unexposed and undeveloped areas of the developed film had a slight yellow haze which did not darken on prolonged exposure to ordinary room illumination.

Example 2

Example 1 was repeated except that 4 moles of Compound 2 described above per mole of silver bromide were utilized in lieu of Compound 1. Without an additional processing, the unexposed and undeveloped areas of the developed film did not darken and remained substantially clear on prolonged exposure to ordinary room illumination. Similar results are obtained when equivalent molar proportions of Compounds 3 to 20 are substituted for Compound 1.

Example 3

Example 1 was repeated except that 2 moles of Compound 8 described above per mole of silver bromide were utilized in lieu of Compound 1. Without additional processing, the unexposed and undeveloped areas of the developed film had a slight yellow cast which did not darken on prolonged exposure to ordinary room illumination.

Example 4

Example 1 was repeated except that 2 moles of Compound 9 described above per mole of silver bromide were utilized in lieu of Compound 1. Without additional processing, the unexposed and undeveloped areas of the developed film had a slight yellow cast which did not darken on prolonged exposure to ordinary room illumination.

Example 5

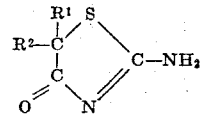
Example 1 was repeated except that 432 grams of Compound 10 described above per mole of silver bromide were utilized in lieu of Compound 1. Without additional processing, the unexposed and undeveloped areas of the developed film did not darken and remained substantially clear on prolonged exposure to ordinary room illumination.

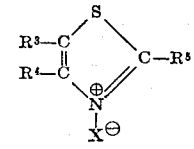
The present invention thus provides new and useful photographic silver halide emulsions, and which emulsions can be stabilized or fixed during development in aqueous alkaline solutions to form chemically and photolytically stable silver derivatives with the unexposed and undeveloped silver halide in the emulsion. No additional or separate fixing step is necessary when processing our emulsions.

The invention has been described in detail with particular reference to 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.

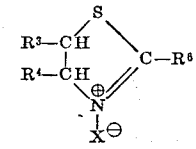
We claim:

1. A photographic silver halide emulsion containing at least one mole per mole of silver halide of a thiazoline derivative having a formula selected from the group consisting of



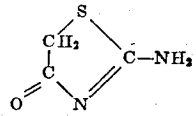


and



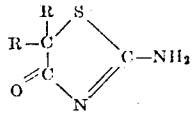
wherein R^1, R^2, R^5 and R^6 are selected from the group consisting of a hydrogen atom, a phenyl radical and an alkyl radical; R^3 and R^4 are selected from the group consisting of a hydrogen atom, a phenyl radical, an alkyl radical, an alkyl radical containing a hydroxyl group and together the necessary carbon and hydrogen atoms to form a phenyl radical; and X, in combination with the adjacent nitrogen atom, is selected from the group consisting of a covalent quaternary salt group containing an electronegative group and an alkyl quaternary salt group including an anion group.

2. A photographic silver halide emulsion containing at least one mole per mole of silver halide of a thiazoline derivative having the formula



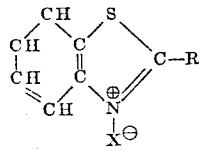
3. A photographic silver halide emulsion containing

at least one mole per mole of silver halide of a thiazoline derivative having the formula



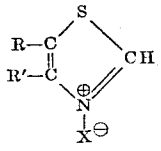
wherein R is an alkyl radical.

4. A photographic silver halide emulsion containing at least one mole per mole of silver halide of a thiazoline derivative having the formula



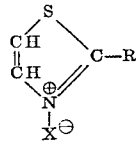
wherein R is an alkyl radical and X, in combination with the adjacent nitrogen atom, is selected from the group consisting of a covalent quaternary salt group containing an electronegative group and an alkyl quaternary salt group including an anion group.

5. A photographic silver halide emulsion containing at least one mole per mole of silver halide of a thiazoline derivative having the formula



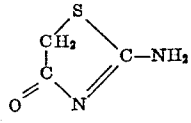
wherein R is a hydroxy substituted alkyl radical, R′ is an alkyl radical and X, in combination with the adjacent nitrogen atom, is selected from the group consisting of a covalent quaternary salt group containing an electronegative group and an alkyl quaternary salt group including an anion group.

6. A photographic silver halide emulsion containing at least one mole per mole of silver halide of a thiazoline derivative having the formula

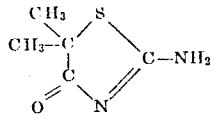


wherein R is an alkyl radical and X, in combination with the adjacent nitrogen atom, is selected from the group consisting of a covalent quaternary salt group containing an electronegative group and an alkyl quaternary salt group including an anion group.

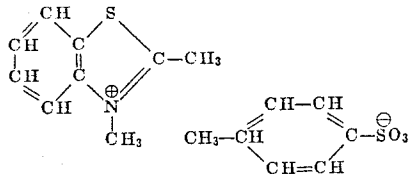
7. A photographic gelatino-silver halide emulsion containing at least one mole per mole of silver halide of a thiazoline derivative having the formula



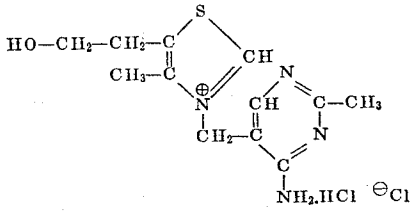
8. A photographic gelatino-silver halide emulsion containing at least one mole per mole of silver halide of a thiazoline derivative having the formula



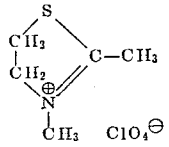
9. A photographic gelatino-silver halide emulsion containing at least one mole per mole of silver halide of a thiazoline derivative having the formula



10. A photographic gelatino-silver halide emulsion containing at least one mole per mole of silver halide of a thiazoline derivative having the formula



11. A photographic gelatino-silver halide emulsion containing at least one mole per mole of silver halide of a thiazoline derivative having the formula



12. A photographic emulsion support having coated thereon an emulsion as described in claim 1.

13. The process for fixing an exposed and developed photographic element as described in claim 12 which comprises treating said element in an aqueous alkaline medium and thereby forming a complex with the thiazoline derivative and unexposed and undeveloped silver halide of said element.

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NORMAN G. TORCHIN, *Primary Examiner.*

HAROLD N. BURSTEIN, *Examiner.*