

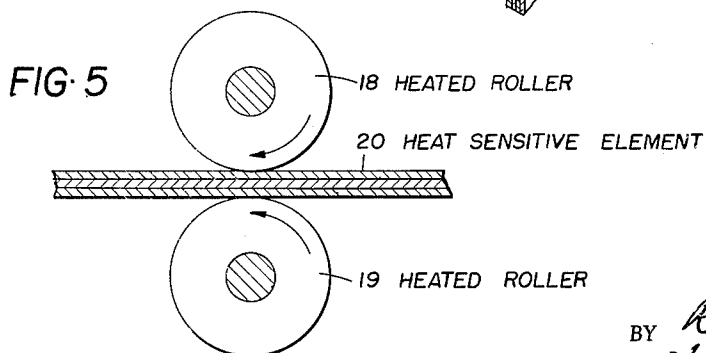
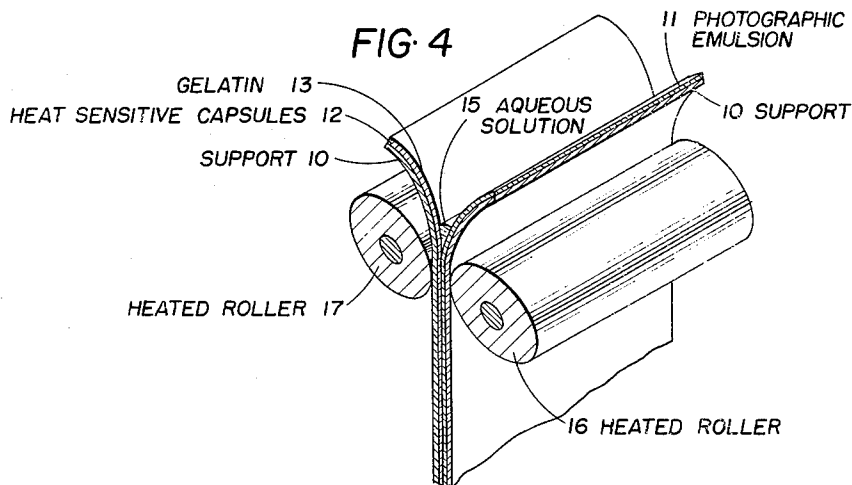
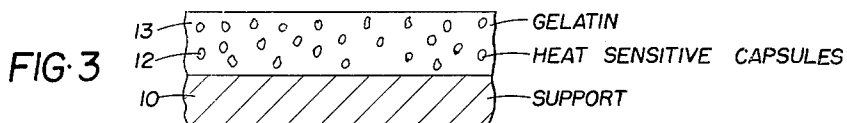
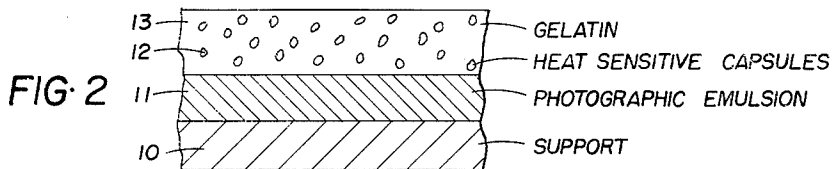
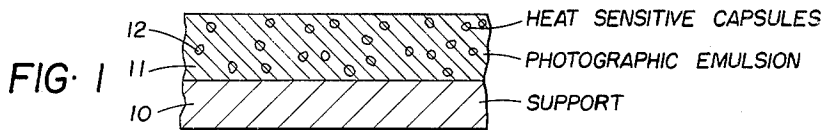
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J. S. YUDELSON ETAL

3,212,896

DRY PROCESSING OF PHOTOGRAPHIC EMULSIONS

Filed June 7, 1961



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3,212,896

DRY PROCESSING OF PHOTOGRAPHIC EMULSIONS

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14 Claims. (Cl. 96-63)

This invention relates to photography and particularly to the dry processing of photographic emulsions. Still more particularly the present invention relates to incorporated thermally sensitive capsules containing photographic processing agents.

In photography, it is the usual procedure to employ liquid processing solutions in the processing of exposed photographic emulsions to form silver images. Liquid processing requires special equipment and usually rather elaborate facilities. According to the present invention, a way has been found in which an exposed photographic emulsion layer can be processed without requiring liquid processing compositions, in fact, the present process is substantially a dry process requiring only the application of mild heat.

It is, therefore, an object of the present invention to provide photographic materials that can be dry processed. Another object is to provide photographic materials having incorporated heat-sensitive capsules containing liquid photographic processing agents. A further object is to provide a dry method of processing such materials. Still another object is to provide a method for preparing the heat-sensitive capsules of the invention and incorporating same in a photographic emulsion layer.

These objects are accomplished by incorporating in silver halide photographic emulsion layers heat-sensitive coacervate-formed capsules containing (1) a photographic processing agent, and (2) a heat decomposable organic nitrogenous compound containing at least one nitrogen-to-nitrogen linkage, said compound being capable of generating gas upon thermal exposure sufficient to burst said capsule and release its internal contents.

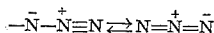
Typical nitrogen-to-nitrogen linkages which unexpectedly were found to be sufficiently gas-producing according to the invention when thermally exposed to temperatures acceptable for use in a photographic application, comprise, for example, a



linkage, a $-N=N-$ linkage, a



linkage, and a



linkage. Organic compounds having nitrogen-to-nitrogen linkages of this type produce copious amounts of nitrogen gas when thermally exposed to a temperature in the range from about 60° C. to about 150° C.

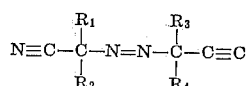
The temperature that can be safely employed in the bursting of capsules incorporated in particular emulsions depends largely upon the emulsion involved. It is well known that some emulsions, depending most usually upon the process used in preparing them and the make-up of the emulsion, are more sensitive to heat than are other emulsions. For example, where the more highly sensitive emulsions are used, a blowing agent of higher thermal sensitivity, i.e., generates gas at a lower temperature, should be used. Similarly, emulsions of lower sensitivity can tolerate high thermal exposures and blowing agents having lower thermal sensitivities can be used.

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To be suitable for use in the present invention, the heat-decomposable substances of this invention should be solid at room temperature and should be inert regarding the capsular wall material and the contents of the capsule. The heat-decomposable substances should not react with the internal contents of the capsule nor should the gas evolved on heat-decomposition react with either the internal contents of the capsule or the surrounding medium. The substances likewise should not interfere chemically with the normal reaction of photographic sensitizers, desensitizers, chemical processing solutions, etc. Moreover the substances should not accelerate nor in any way substantially affect the normal processing of photographic reactions. Still further the heat decomposable substances should be non-toxic and odorless, as should their decomposition products. The substances and their decomposition products should also be substantially colorless, since their use in the manufacture of many types of photographic materials include those which must be light in color and free of stain. The heat decomposable substances of this invention will be referred to herein as "blowing" agents. For use in the invention these agents should be miscible in water-immiscible solvents. Solvents of this type include the natural occurring oils such as olive oil, i.e., coconut oil, castor oil, fish oils; animal oils such as sperm oil; vegetable oil; mineral oils, such as petroleum lubricating oil; synthetic compounds such as chlorinated diphenyl, methylsalicylate, di-n-butylphthalate, etc. Other suitable solvents are disclosed in U.S. Patent 2,800,457, patented July 23, 1957.

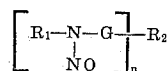
Suitable heat-decomposable organic substances having a nitrogen-to-nitrogen linkage according to the present invention comprise the following classes of compounds.

A. Azobis (alkanenitriles) as represented by the following general formula:



wherein R_1 , R_2 , R_3 , and R_4 can each represent a hydrogen atom, a lower alkyl group containing from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, etc., an aryl group such as phenyl, naphthyl, and a substituted aryl group having substituents such as amino (NH_2), a halogen atom, such as chlorine, bromine, etc., a lower alkyl group having from 1 to 4 carbon atoms such as methyl, ethyl, propyl, isopropyl, etc., and a lower alkoxy group, such as methoxy, ethoxy, etc.

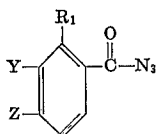
B. N-nitroso-N-alkylalkaneamides and N-nitroso-N-alkylalkanesulfonamides having the general formula:



wherein G is $-CO-$ or $-SO_2-$, R_2 is a lower alkyl group having from 1 to 4 carbon atoms, and n is the integer, 1 or 2. When n is 1, R_1 can represent an alkyl group having from 3 to 10 carbon atoms; an aryl group such as phenyl, naphthyl; a substituted aryl group having substituents such as a halogen atom (e.g. chlorine, bromine), and a lower alkoxy group such as methoxy, ethoxy, etc. When n is 2, R_1 represents an alkylene group having from 3 to 10 carbon atoms; an arylene group such as phenylene, naphthylene; a substituted arylene group having substituents such as a halogen atom (e.g., chlorine, bromine), a lower alkyl group having from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, etc., and a lower alkoxy group, such as methoxy, ethoxy, etc.

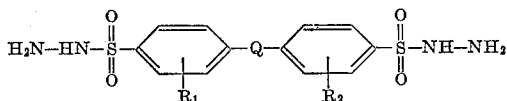
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C. Aryl azides having the general formula:



wherein R_1 represents a hydrogen atom; a hydroxyl group; a halogen atom (e.g., chlorine, bromine, etc.); an amino group; a lower alkyl group having from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, etc.; a lower alkoxy group having from 1 to 4 carbon atoms, such as methoxy, ethoxy, etc.; Y and Z can each represent a hydrogen atom; a hydroxyl group; an alkyl group containing from 1 to 4 carbon atoms, Y and Z together can represent the atoms necessary to complete a benzene ring, and Y and Z together can represent the atoms of a benzene ring which can have substituents thereon such as an amino group; a lower alkyl group having from 1 to 4 carbon atoms; a hydroxyl group, etc.

D. Disulfonhydrazide such as bi(aryl)-p,p'-disulfonhydrazide having the general formula:



wherein R_1 and R_2 can each represent a hydroxyl group; a halogen atom (e.g., chlorine, bromine, etc.); a lower alkyl group having from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, etc.; a lower alkoxy group having from 1 to 4 carbon atoms, such as methoxy, ethoxy, etc.; and Q can represent a sulfur atom, an oxygen atom, a $(-CH_2-)_n$ group wherein n is an integer from 1 to 10, and a



group wherein each R_3 and R_4 comprise an alkyl radical having from 1 to 10 carbon atoms.

Other heat-decomposable substances which are gas-producing when thermally exposed comprise certain diazonium salts such as those described in U.S. Patents 2,908,572, October 13, 1959; 2,822,271, February 4, 1958; and 2,805,159, September 3, 1957.

Certain organic peroxides are also gas-producing when thermally exposed. These include benzoyl peroxide, acetylbenzoyl peroxide and di(tertiary alkyl) peroxide. These peroxides and others are disclosed in U.S. Patents 2,403,758, July 9, 1946; 2,381,561, August 7, 1954; 2,160,903, June 6, 1939; and 2,109,595, March 1, 1938.

Photographic processing solutions and other materials used in a photographic application according to the present invention and which are encapsulated along with blowing agents of this invention should likewise be miscible in water-immiscible solvents. Typical photographic developers of this type include, for example, 4-phenyl catechol, 4,4 - dimethyl - 3 - phenyl-3-pyrazolidone; octadecyloxybenzaldehyde Schiff base of N-ethyl-N-hydroxyethyl-p-phenylenediamine; and the like. Other photographic processing agents which can be encapsulated along with a blowing agent of this invention include β -carboxymethyl mercaptobenzal acetophenone, benzotriazole, etc.

By employing a rapid encapsulation process, water soluble processing agents can also be utilized, such as hydroquinone, particularly when suspended in a viscous water-immiscible solvent.

In preparing the capsules of this invention, a hydrophilic colloid is used which possesses the ability to disperse a water-immiscible solvent. The capsules incorporating the blowing agents and photographic compounds of the invention are formed essentially by a process com-

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prising coacervation. Suitable processes of this type have been described in U.S. Patent 2,800,457, issued July 23, 1957. One of such processes which has particular relevance to the present invention will be described in the following paragraph.

In this invention, a suitable blowing agent and an oil-soluble or oil-dispersible photographically employed compound are mixed thoroughly in a water-immiscible solvent. In the case where either or both the addenda are dispersed in the water-immiscible solvent, i.e., oil, such addenda should be colloidal in size. The water-immiscible solvent containing the addenda is then dispersed in a hydrophilic colloid such as gum arabic. The dispersion is then mixed with an aqueous sol of another colloid such as pigskin gelatin. Encapsulation of the water-immiscible solvent containing the blowing agent and photographically employable material then results when the dispersion is diluted with water at a certain pH. Thereafter the capsules can be gelled by treatment with cold water or by keeping in a cold environment. The suspension of capsules can be concentrated or diluted with water-soluble binders, etc., so that mixtures prepared thereby can be used according to processes of the present invention. Typical substances that can be incorporated in the capsules according to the present invention comprise, for example, photographic processing reagents, such as developers, fixers, combined developers and fixers, etc.; color-forming compounds such as color-couplers, etc.; color-producing substances such as dyes; color-producing components of dyes; photographic sensitizers, photographic desensitizers, etc.

The heat-sensitive capsules of the present invention can also be employed in a processing web whereby the web is placed in thermal contact with a photographic emulsion layer to be processed. Webs of the type contemplated can be prepared by coating on a support heat-sensitive capsules suspended in a suitable binder such as gelatin, synthetic resins, and the like. In a process of this type, the web is normally placed in contact with the exposed emulsion layer and the two-ply assembly passed between heated rollers to give the required thermal exposure. After allowing sufficient time for the particular processing step involved to take place, the emulsion layer is removed from the web and the next processing step carried out.

One manner in which the heat-sensitive capsules of our invention can be employed in a photographic application will be further illustrated by reference to the accompanying drawings. In FIG. 1 thereof is shown a sectional view of a support 10 coated with a silver halide photographic emulsion layer 11 containing heat-sensitive capsules 12 uniformly dispersed throughout the emulsion layer. In FIG. 2 is shown a sectional view of a silver halide emulsion layer 11 coated on a support 10 wherein the emulsion layer 11 is overcoated with a gelatin layer 13 which has uniformly distributed therethrough heat-sensitive capsules 12. FIG. 3 of the accompanying drawing shows a support 10 coated with a gelatin layer 13 and having uniformly distributed therethrough heat-sensitive capsules 12. The heat-sensitive element of FIG. 3 is a non-light-sensitive element or web and can be used in the processing of photographic materials.

FIG. 4 of the accompanying drawing shows a manner of treating a silver halide photographic emulsion layer with a non-light-sensitive element as shown in FIG. 3. In FIG. 4 a silver halide emulsion layer 11 coated on a support 10 is pressed into heat contact with a heat-sensitive layer 13 coated on a support 10 and having the heat-sensitive capsules 12 uniformly dispersed therethrough. At the interface between the photographic element and the treating element of FIG. 4 an aqueous solution 15 is provided so that sufficient water is assured in carrying out the process. The emulsion element and the treating element as shown in FIG. 4 are passed in pressure contact between heated rollers 16 and 17.

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In FIG. 5 is shown a pair of heated rollers 18 and 19 which provide heat for the rupturing of the capsules contained in element 20. The element 20 of FIG. 5 can be a heat-sensitive element as shown in FIGS. 1 and 2 of the accompanying drawing or the apparatus of FIG. 5 can be utilized to provide the heat required where a conventional silver halide emulsion layer is processed with a heat-sensitive element as shown in FIG. 3. It is apparent also that, by providing a pair of rollers in tandem, different processing temperatures can be provided. For example, by incorporating into the heat-sensitive layer capsules of both fixer and developer and by contacting such a heat-sensitive element with a photographic layer to be processed, the first pair of rollers could provide the temperature required to burst the capsules containing a developer and the second pair of rollers, which would be in tandem arrangement with the first, could be provided with a temperature sufficient to burst the capsules containing a photographic fixer. It will be apparent that a wide variety of applications can be made of the present invention.

The invention will now be described by reference to the following examples.

Example 1

To 45 ml. of polyglycol (11-200 Dow Chemical Company) formed by the condensation of glycerol and propylene oxide and having a molecular weight of about 2700, was added 5 grams of 4-phenylcatechol and 2 grams of p,p'-oxy-bis(benzene sulfonyl hydrazide). The solution was then dispersed in 80 grams of 11.1 percent gum arabic and emulsified for 10 minutes, at the end of which time the droplet size varied from about 0.7 to about 5 microns. The dispersion was then added to 80 grams of an 11.1 percent solution of pigskin gelatin, the pH of which was adjusted so that the final pH of the mixture was 4.7 to 5.0. The temperature was kept at 50 to 55 degrees C. While rapidly stirring the mixture, 178 ml. of water was added. The mixture, while being continuously agitated, was then added to a rapidly agitated cold water bath which contained about 2.5 liters and was held at a temperature of 3 to 5 degrees C. The highly swollen coacervate gelled around each oil droplet. A minute amount of an anti-foaming agent (SS-60—General Electric Company) was added to the chilled bath before the addition of the coacervate to eliminate foaming. The mixture was then stirred for approximately 30 minutes to assure separation of each capsule. The capsules were then hardened by the adding of 40 grams of a 25 percent aqueous glutaraldehyde solution and stirring for three hours. A 10 percent sodium acetate solution was then added to the suspension while stirring until coagulation occurred. The coagulum was then washed for three hours with cold water. The wet coagulum was then drained of excess water and stored, until ready for addition to a silver halide emulsion prepared as follows:

Solutions were made of (A) 25 grams of gelatin in 1 liter of water at 40° C. (B) 100 grams silver nitrate in 500 ml. water at 20° C. and (C) 35 grams of sodium chloride in 365 ml. of water. Solutions B and C were run simultaneously into solution A at a uniform rate while stirring the latter over a period of about 10 minutes; solution B was not allowed to run in faster than C. The solution was then stirred continuously with mild agitation while holding at 40° C.

For addition to the silver halide emulsion dispersion, 50 grams of the coagulum of paragraph 1 of this example was mixed with 75 ml. of hot water, 10 ml. of a 7 percent gelatin solution, and two drops of an antifoaming agent (SS-60—General Electric Company). The mixture was then dispersed with a Waring Blendor for 20 seconds and added to the emulsion solution while stirring. By adding the coagulum preparation slowly to the emulsion solution while stirring, the capsules became dispersed uniformly throughout the emulsion.

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The emulsion was then coated on cellulose acetate film base over an area of about 500 square feet and dried. The film was exposed to a subject by contact with a negative having opaque areas and clear areas. Thereafter the exposed element containing the encapsulated developing agent in the emulsion layer was passed between a pair of heated rollers to give an internal temperature of at least 80° C. The exposed and developed emulsion layer was fixed in a conventional manner to produce a positive image of good quality.

Example 2

To 45 ml. of a 5 percent solution of azo-bis(isobutyronitrile) in di-n-butylphthalate was added 5 grams of 4,4-dimethyl-3-phenyl-3-pyrazolidone which was then dispersed into 80 grams of 11.1 percent gum arabic and emulsified until the droplet size varied from about 0.8 to about 6 microns. The dispersion was then added to 80 grams of 11.1 percent solution of gelatin at a temperature of 45 to 50° C. The pH was adjusted to 4.8. While rapidly stirring, 178 ml. of water was added to the mixture. The mixture was then added to 3 liters of cold (5° C.) water in order to gel the coacervate. The capsules were hardened by the addition of 40 grams of a 25 percent aqueous glutaraldehyde solution to the suspension and stirred for three hours. The suspension was then coagulated by means of sodium acetate after which the coagulum was washed for three hours with cold water. After draining to remove excess water, 50 grams of the coagulum was mixed with 75 ml. of hot water, 10 ml. of a 7 percent gelatin solution and 2 drops of GE SS-60 Anti-Foaming Agent. The mixture was dispersed with a Waring Blendor for 20 seconds, then mixed with 0.3 ml. of a 2 percent solution of Duponol dispersing agent, and coated on a gelatin subbed cellulose acetate film base to give a coverage of 3.1 grams per square foot. The coating consisted of closely-packed capsules which adhered to each other by virtue of partial fusion of their walls. A small amount of gelatin was added to disperse the capsules and also bind the capsules together in the dried film.

Strips of Kodabromide Paper were then given a suitable exposure, and pressed in heat contact (at a temperature of about 90° C.) with the developer-capsule web prepared according to the description in the above paragraph. After about a two-minute interval the capsular web was removed from the emulsion layer of the exposed photographic paper. The paper was then fixed in a conventional manner to reveal a high-quality warm-tone photographic negative image.

Example 3

A 4 percent Aroclor #1232 solution of 2-carbazido-1-naphthol was made. (The colorless chlorinated hydrocarbon solvent, Aroclor #1232, was purchased from Monsanto Company.) To the solution was added Sudan III colorant at a 1.0 percent concentration. The mixture was then encapsulated, hardened, separated, and drained of excess water according to the method described in Example 1.

The capsules were then dispersed in a 7 percent gelatin solution to which was added 15 percent (based on weight of the gelatin) of a plasticizer, bis(2-(2-methoxyethoxy) ethyl) ether. The ratio of the capsules to gelatin was 2:1 by weight. The mixture was then coated on a strip of Kodak Verifax copy paper and given a thermographic exposure in surface contact with a printed original. A short exposure reproduced a copy of the original on the copy paper.

Similar results were obtained using 2-carbazido-1-acetoxy-naphthalene.

Example 4

To a 10 percent solution of N,N'-dinitroso-N,N'-dimethylglutaramide in Aroclor #1232 solvent, 20.0 grams per liter of β -carboxymethyl mercapto benzalacetophen-

none fixing agent was added. The solution was then encapsulated, hardened, separated and drained of excess water as in Example 1.

75 grams of the capsules prepared according to the above paragraph and containing the blowing agent and water-insoluble fixing agent was dispersed in a silver halide emulsion prepared as in Example 1. The mixture was then dispersed with a Waring Blendor for 20 seconds and then added to the emulsion solution as in Example 1.

After coating the emulsion on cellulose acetate film base in a conventional manner and exposing to a negative image, the exposed element containing the encapsulated blowing agent and fixing agent was developed in a photographic developer of the following composition:

N-methyl-p-aminophenolsulfate	-----grams--	2.2
Hydroquinone	-----do----	8.8
Sodium sulfite (anhydrous)	-----do----	72.0
Sodium carbonate (monohydrate)	-----do----	130.0
Potassium bromide	-----do----	4.0
Water to make	-----liter--	1.0

After developing, the element was washed and passed between a pair of heated rollers. After washing, a developed and fixed negative image of good quality resulted.

The N,N'-dinitroso-N,N'-dimethylglutaramide was prepared by the nitrosation of N,N'-dimethylglutaramide, which in turn was made by reacting methylamine with N,N'-dimethylglutarate.

Similar results were obtained using N,N'-dinitroso-N,N'-dimethylsuccinamide prepared by the nitrosation of N,N'-dimethylsuccinamide.

In the present invention, the blowing agents employed evolve copious amounts of gas when exposed to a temperature in the range from about 60° C. to about 150° C. Ordinarily an exposure temperature in the range from about 70° C. to about 130° C. results in copious gas being evolved by the blowing agents. Accordingly, in this comparatively narrow temperature range, the optimum temperature for processing can be reached easily and quickly by a number of ways. For example, passing the processing element between a pair of heated rollers, heating on a hot plate, etc., can give good results. In certain cases it may be advantageous to expose a photographic element or a document reproducing element incorporating the heat-sensitive capsules of this invention to infrared radiation such as that provided by a thermographic exposure. Naturally, the more suitable means for any particular application of this invention would need to be selected for the particular processing or development step contemplated. In any event, as shown above, the incorporation of at least one of the blowing agents of this invention gave substantially immediate and complete rupturing of the capsule so that it was necessary to maintain the elevated temperature for only a very brief period.

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 scope and spirit of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A photographic element comprising a silver halide emulsion and integral therewith a water-permeable, hydrophilic colloid layer on a support, said layer comprising

(1) a continuous phase of water-permeable, hydrophilic colloid, and uniformly dispersed throughout said continuous phase,

(2) a discontinuous phase of heat sensitive capsules each comprising a core containing

(a) a solution in an oily, water-immiscible solvent of a silver halide processing reagent selected from the group consisting of silver halide photo-

graphic developers, fixers, and combined developers and fixers,

(b) a heat-decomposable, gas-producing, organic compound compatible with silver halide photographic emulsions, having at least 2 nitrogen atoms linked together, said nitrogen atoms being liberated by heat at a temperature of about 60° C. to about 150° C. to produce nitrogen gas, and

(c) surrounding said core, a shell of a gelatin-gum arabic coacervate.

2. A photographic silver halide emulsion layer on a support, said layer comprising

(1) a continuous phase of organic water-permeable hydrophilic colloid containing light-sensitive silver halide salts and uniformly dispersed throughout said continuous phase,

(2) a discontinuous phase of heat sensitive capsules each comprising a core containing

(a) a solution in an oily, water-immiscible solvent of a silver halide processing reagent selected from the group consisting of silver halide photographic developers, fixers, and combined developers and fixers,

(b) a heat-decomposable, gas-producing, organic compound compatible with silver halide emulsions, having at least 2 nitrogen atoms linked together, said nitrogen atoms being liberated by heat at a temperature of about 60° C. to about 150° C. to produce nitrogen gas, and

(c) surrounding said core, a shell of a gelatin-gum arabic coacervate.

3. A water-permeable, hydrophilic colloid layer on a support, said layer comprising

(1) a continuous phase of water-permeable, hydrophilic colloid, and uniformly dispersed throughout said continuous phase,

(2) a discontinuous phase of heat sensitive capsules each comprising a core containing

(a) a solution in an oily, water-immiscible solvent of at least one silver halide processing reagent selected from the group consisting of silver halide photographic developers, fixers, and combined developers and fixers,

(b) a heat-decomposable, gas-producing, organic compound compatible with silver halide photographic emulsions, having at least 2 nitrogen atoms linked together, said nitrogen atoms being liberated by heat at a temperature of about 60° C. to about 150° C. to produce nitrogen gas, and

(c) surrounding said core, a shell of a gelatin-gum arabic coacervate.

4. A water-permeable, hydrophilic colloid layer on a support, said layer comprising

(1) a continuous phase of water-permeable, hydrophilic colloid and uniformly dispersed throughout said continuous phase,

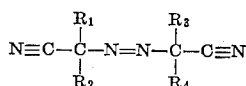
(2) a discontinuous phase of heat sensitive capsules each comprising a core containing

(a) a solution in an oily, water-immiscible solvent of at least one silver halide photographic processing reagent selected from the group consisting of silver halide photographic developers, fixers, and combined developers and fixers,

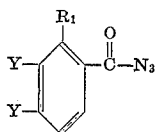
(b) a heat-decomposable, gas-producing, organic compound compatible with silver halide photographic emulsions, having at least 2 nitrogen atoms linked together, said nitrogen atoms being liberated by heat at a temperature of about 60° C. to about 150° C. to produce nitrogen gas, said compounds being selected from the

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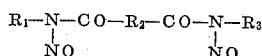
class consisting of azobis(alkanenitriles) as represented by the following formula:



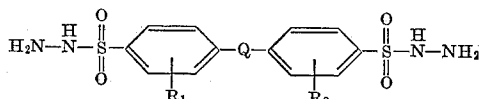
wherein R₁, R₂, R₃ and R₄ each represents hydrogen, lower alkyl containing from 1 to 4 carbon atoms, phenyl and a substituted aryl group having substituents selected from the group consisting of halogen, lower alkyl having from 1 to 4 carbon atoms and lower alkoxy having from 1 to 4 carbon atoms; carbazido-aryl compounds having the following formula:



wherein R₁ represents a member from the group consisting of hydrogen, hydroxyl, halogen, lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms, Y and Z each represents hydrogen, hydroxyl and alkyl containing from 1 to 4 carbon atoms, Y and Z together represent the atoms of a benzene ring having substituents thereon selected from the group consisting of lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms, halogen and hydroxyl; N-nitroso compounds having the following formula:



wherein R₁ and R₃ each represents alkyl having from 1 to 4 carbon atoms and R₂ represents alkylene having from 3 to 10 carbon atoms; and bis-phenolsulfonyl hydrazide having the following formula:



wherein R₁ and R₂ each represents hydroxyl, halogen, lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms and Q is selected from the group consisting of sulfur, oxygen and alkylene having from 1 to 10 carbon atoms, and

(c) surrounding said core, a shell of a gelatin-gum arabic coacervate.

5. A photographic element comprising a silver halide emulsion on a support and integral therewith a water-permeable hydrophilic colloid layer, said layer comprising

(1) a continuous phase of water-permeable, hydrophilic colloid, and uniformly dispersed throughout said continuous phase,

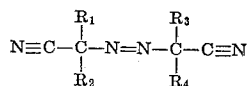
(2) a discontinuous phase of heat sensitive capsules each comprising a core containing

(a) a solution in an oily, water-immiscible solvent of at least one silver halide photographic processing reagent selected from the group consisting of silver halide photographic developers, fixers, and combined developers and fixers,

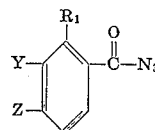
(b) a heat-decomposable, gas-producing, organic compound compatible with silver halide photographic emulsions, having at least 2 nitrogen atoms linked together, said nitrogen atoms being liberated by heat at a temperature of about 60° C. to about 150° C. to produce nitrogen gas, said compounds being selected from the class

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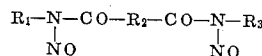
consisting of azobis(alkanenitriles) as represented by the following formula:



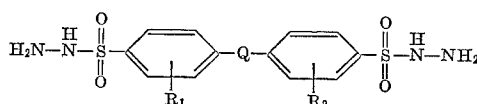
wherein R₁, R₂, R₃ and R₄ each represents hydrogen, lower alkyl containing from 1 to 4 carbon atoms, phenyl and a substituted aryl group having substituents selected from the group consisting of halogen, lower alkyl having from 1 to 4 carbon atoms and lower alkoxy having from 1 to 4 carbon atoms; carbazido-aryl compounds having the following formula:



wherein R₁ represents a member from the group consisting of hydrogen, hydroxyl, halogen, lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms, Y and Z each represents hydrogen, hydroxyl and alkyl containing from 1 to 4 carbon atoms, Y and Z together represent the atoms of a benzene ring having substituents thereon selected from the group consisting of lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms, halogen and hydroxyl; N-nitroso compounds having the following formula:



wherein R₁ and R₃ each represents alkyl having from 1 to 4 carbon atoms and R₂ represents alkylene having from 3 to 10 carbon atoms; and bis-phenolsulfonyl hydrazide having the following formula:



wherein R₁ and R₂ each represents hydroxyl, halogen, lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms and Q is selected from the group consisting of sulfur, oxygen and alkylene having from 1 to 10 carbon atoms, and

(c) surrounding said core, a shell of a gelatin-gum arabic coacervate.

6. A photographic silver halide emulsion layer on a support, said layer comprising

(1) a continuous phase of water-permeable, hydrophilic colloid and uniformly dispersed throughout said continuous phase,

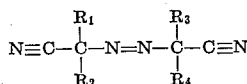
(2) a discontinuous phase of heat sensitive capsules each comprising a core containing

(a) a solution of an oily, water-immiscible solvent of at least one silver halide photographic processing reagent selected from the group consisting of silver halide photographic developers, fixers and combined developers and fixers,

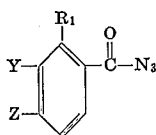
(b) a heat-decomposable, gas-producing, organic compound compatible with silver halide photographic emulsions, having at least 2 nitrogen atoms linked together, said nitrogen atoms being liberated by heat at a temperature of about 60° C. to about 150° C. to produce nitrogen gas, said compounds being selected from the class

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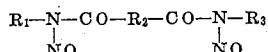
consisting of azobis(alkanenitriles) as represented by the following formula:



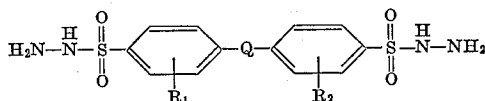
wherein R_1 , R_2 , R_3 and R_4 each represents hydrogen, lower alkyl containing from 1 to 4 carbon atoms, phenyl and a substituted aryl group having substituents selected from the group consisting of halogen, lower alkyl having from 1 to 4 carbon atoms and lower alkoxy having from 1 to 4 carbon atoms; carbazido-aryl compounds having the following formula



wherein R_1 represents a member from the group consisting of hydrogen, hydroxyl, halogen, lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms, Y and Z each represents hydrogen, hydroxyl and alkyl containing from 1 to 4 carbon atoms, Y and Z together represent the atoms of a benzene ring having substituents thereon selected from the group consisting of lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms, halogen and hydroxyl; N-nitroso compounds having the following formula:



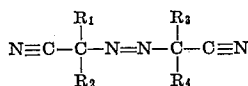
wherein R_1 and R_2 each represents alkyl having from 1 to 4 carbon atoms, and R_3 represents alkylene having from 3 to 10 carbon atoms; and bis-phenolsulfonyl hydrazide having the following formula:



wherein R_1 and R_2 each represents hydroxyl, halogen, lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms and Q is selected from the group consisting of sulfur, oxygen and alkylene having from 1 to 10 carbon atoms, and

(c) surrounding said core, a shell of a gelatining arabic coacervate.

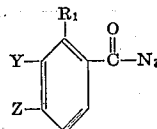
7. A hydrophilic colloid layer of claim 1 wherein said gas-producing organic compound is selected from the class of compounds comprising azobis(alkanenitriles) as represented by the following formula:



wherein R_1 , R_2 , R_3 and R_4 each represents hydrogen, lower alkyl containing from 1 to 4 carbon atoms, phenyl and substituted aryl having substituents selected from the group consisting of halogen, lower alkyl having from 1 to 4 carbon atoms and lower alkoxy having from 1 to 4 carbon atoms.

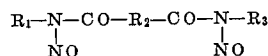
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8. A hydrophilic colloid layer of claim 1 wherein said gas-producing compound is a carbazido-aryl compound having the formula:



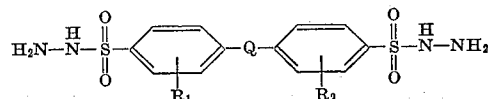
wherein R_1 represents a member from the group consisting of hydrogen, hydroxyl, halogen, lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms, Y and Z each represents hydrogen, hydroxyl and alkyl containing from 1 to 4 carbon atoms, Y and Z together represent the atoms necessary to complete a benzene ring having substituents thereon selected from the group consisting of lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms, halogen and hydroxyl.

9. A hydrophilic colloid layer of claim 1 wherein said gas-producing compound is a N,N'-dinitroso-N,N'-dialkylalkylamide having the formula:



wherein R_1 and R_3 each represents alkyl having from 1 to 4 carbon atoms and R_2 represents alkylene having from 3 to 10 carbon atoms.

10. A hydrophilic colloid layer of claim 1 wherein said compound is a bis-phenolsulfonyl hydrazide having the formula:



wherein R_1 and R_2 each represents hydroxyl, halogen, lower alkyl having from 1 to 4 carbon atoms, lower alkoxy having from 1 to 4 carbon atoms, and Q is selected from the group consisting of sulfur, oxygen and alkylene having from 1 to 10 carbon atoms.

11. Heat sensitive capsules formed by the steps comprising

- (1) making a solution of water-immiscible solvent containing at least one silver halide photographic reagent selected from the group consisting of silver halide photographic developers, fixers and combined developers and fixers and a heat-decomposable, gas-producing, organic compound compatible with silver halide photographic emulsions, having at least 2 nitrogen atoms linked together, which decomposes at a temperature at about 60° C. to about 150° C. to release nitrogen gas,
- (2) making an aqueous sol of gum arabic,
- (3) emulsifying in said sol, the said water-immiscible solvent,
- (4) adding and stirring into the emulsion an aqueous sol of pigskin gelatin, and
- (5) adding sufficient water to bring the emulsion into the coacervate region defined by the occurrence of the formation of said capsules.

12. A process of obtaining a silver image from an exposed silver halide emulsion comprising contacting the exposed silver halide emulsion against a water-permeable, hydrophilic colloid layer on a support, said layer comprising

- (1) a continuous phase of water-permeable, hydrophilic colloid and uniformly dispersed throughout said continuous phase,
- (2) a discontinuous phase of heat sensitive capsules each comprising a core containing
 - (a) a solution in an oily, water-immiscible solvent of at least one silver halide photographic developer,

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- (b) a heat-decomposable, gas-producing, organic compound compatible with silver halide emulsions, having at least 2 nitrogen atoms linked together, said nitrogen atoms being liberated by heat at a temperature of about 60° C. to about 150° C. to produce nitrogen gas, and

- (c) surrounding said core, a shell of a gelatin-gum arabic coacervate,

thermally treating the exposed silver halide emulsion in contact with the said hydrophilic colloid layer to a temperature in the range from about 60° C. to about 150° C. for a sufficient time to burst the said heat sensitive capsules and stabilizing the silver halide emulsion.

13. A process of obtaining the silver image from an exposed silver halide emulsion on a support and having integral with the emulsion a water-permeable, hydrophilic colloid layer, said layer comprising

- (1) a continuous phase of water-permeable, hydrophilic colloid and uniformly dispersed throughout said continuous phase,

- (2) a discontinuous phase of heat sensitive capsules each comprising a core containing

- (a) a solution in an oily, water-immiscible solvent of at least one silver halide photographic developer,

- (b) a heat-decomposable, gas-producing, organic compound compatible with silver halide photographic emulsions, having at least 2 nitrogen atoms linked together, said nitrogen atoms being liberated by heat at a temperature of about 60° C. to about 150° C. to produce nitrogen gas, and

- (c) surrounding said core, a shell of a gelatin-gum arabic coacervate,

by heating the exposed silver halide emulsion to a temperature in the range from about 60° C. to about 150° C. for a sufficient time to burst the said heat sensitive capsules and the silver halide emulsion.

14. A process of obtaining a silver image from an exposed silver halide emulsion layer comprising

- (1) a continuous phase of organic water-permeable hydrophilic colloid containing light sensitive silver halide salts and uniformly dispersed throughout said continuous phase,

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- (2) a discontinuous phase of heat sensitive capsules each comprising a core containing

- (a) a solution of an oily, water-immiscible solvent of at least one silver halide photographic developer,

- (b) a heat-decomposable, gas-producing, organic compound compatible with silver halide photographic emulsions, having at least 2 nitrogen atoms linked together, said nitrogen atoms being liberated by heat at a temperature about 60° C. to about 150° C. to produce nitrogen gas, and

- (c) surrounding said core, a shell of gelatin-gum arabic coacervate,

by heating the exposed silver halide emulsion to a temperature in the range from about 60° C. to about 150° C. for a sufficient time to burst the said heat sensitive capsules and stabilizing the silver halide emulsion.

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