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3,275,443

ANTI-FOGGING AGENTS FOR AN N-VINYL, ORGANIC HALOGEN, DYE FORMER SYSTEM

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This invention relates to compositions which are sensitive to light and which are suitable for photography and to the use of such compositions. More particularly the invention relates to an improvement in the compositions described in my United States Patents 3,042,517, 3,042,518, and 3,042,519 and 3,046,125.

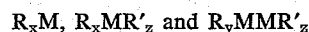
The photographic process described in the above United States patents involve the imagewise exposure to light or to light and heat of compositions comprising various kinds of N-vinyl compounds and various kinds of halogen containing organic compounds, usually dispersed in or disposed on a substrate such as a film forming plastic material, including paper, cloth, or other plastic material. A latent image forms as a result of the imagewise exposure and further exposure to heat or infrared radiation is utilized to render the latent image visible, again as described in the above patents.

In practicing the inventions described in the aforesaid United States patents it has been found that when very low exposures are utilized, the heating incident to developing a visible image is occasionally sufficient to overheat the composition and to cause fogging of the same. While I do not wish to be bound by any specific theory, it appears that the use of heat or infrared energy in the development of a visible image may be accompanied by a thermal reaction between the N-vinyl compound and the halomethane or halogen containing compound which begins to be evident at a temperature slightly higher than the optimum for development purposes and this thermal reaction results in a color similar to the image color produced as the result of the intended exposure and development. For example, if a light unexposed mixture of carbon tetrabromide and N-vinyl carbazole is heated at 160° C. for about 1 minute in the absence of light a brownish color develops. This formation of brownish color would appear to indicate a thermal degradation of a mixture of a halomethane compound and N-vinyl compound taking place at a temperature level or degree of thermal energy absorption considerably higher than that which would be encountered during storage or at the ordinarily prevailing temperatures previously utilized for development of such compositions. Thus in a low light exposure image, a competition between image development and onset of fog would appear to exist. As a consequence, if the thermal treatment is not carefully controlled, or if the conditions of exposure are such that an extensive thermal treatment is required, it is possible that the desired image may be lost through fogging of the background as indicated in my United States Patent 3,042,517.

A principal object of this invention is the modification of the compositions described in the above patents in a manner which entirely eliminates the possibility of fogging due to thermal treatment of said compositions, no matter how extensive the thermal treatment, whereby even very faint images may be distinguished without difficulty from the background regardless of the extent of thermal development.

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This and other objects of the invention are accomplished by the addition of one or more compounds represented by one of the following general formulas:



wherein M represents an element selected from the group consisting of the elements forming the right hand members of Groups IV and V of the Periodic Table of the Chemical Elements, namely: germanium, tin, lead, phosphorus, arsenic, antimony, and bismuth; R is selected from the group consisting of aryl and alkaryl; R' is selected from the group consisting of alkyl, aryl, alkaryl and aralkyl and R and R' may each represent more than 1 kind of radical in any compound; and x, y, and z are integers from 1 to 4 such that the total number of R and R' organic radicals is sufficient to satisfy the valence of the element M in the compounds. Again, while I do not wish to be bound to any specific theory, the inference is that on thermal treatment of the composition these metallo-organic compounds react either with the halomethane compound or a product of light decomposition of the halomethane compound to produce a material which is incapable of reacting thermally with the N-vinyl compound within the temperature limits normally used for development. The basis for this statement is that on heating the N-vinyl compound alone in the absence of light and under a protective atmosphere such as nitrogen that no change in color of any major extent takes place on prolonged heating even though a thermal polymerization reaction has developed to produce a substantially colorless resinous material.

Each of the fog eliminators suitable in the practice of the present invention exhibits a melting point substantially above room temperature, that is, it is normally a solid at room temperature; exhibits a ready solubility in various organic solvents; and is characterized by a freedom from halogens or any elements other than C, H and M.

Briefly the photosensitive compositions of this invention comprise the following:

Constituent:	Parts by weight
N-vinyl compound	10 to 200
Polyhalogen compound (free radical source)	10 to 200
Fog eliminator compound	0.1 to 10

In the compositions of this invention, the N-vinyl compound is preferably one of those listed in Table I of U.S. 3,042,519 and includes N-vinyl carbazole, N-vinyl indole, N-vinyl phenyl naphthylamine, N-vinyl pyrrole, N-vinyl diphenylamine and N-vinyl imides or N-vinyl amides of the kinds described in the above patents. Preferably the N-vinyl compounds is one in which the vinyl group is attached to a nitrogen atom in a five or six membered heterocyclic ring.

The polyhalogen compounds of the compositions are normally solid compounds in which three halogen atoms are attached to a terminal carbon atom. Preferably these halogens are bromine atoms. Preferred poly-halogen compounds which act as free radical sources are carbon tetrabromide, pentabromomethane, hexabromomethane, hexachlorethane, benzyltribromide ($C_6H_5CBr_3$), α,α,α -tribromoacetophenone, and α,α,α -tribromoacetamide.

Typical fog eliminators are listed in Table I, below. It appears that the compounds listed in Table I vary in effectiveness with respect to the amounts required to produce the desired result roughly in accordance with the atomic weight of the element (M) attached to the aryl

nucleus and also its atomic percentage. For example, in the series of compounds represented by the triphenyl compounds of P, As, Sb and Bi, the amount of compound required to produce equal effects varies directly with the molecular weight of the compound, and with the amount of metal atom present in the compound, and particularly the amount of metal attached to an aryl substituent. For example, in the specific procedure as defined in Example 2 and relating to the range of concentrations given above, it is found that the maximum concentration of the triphenylphosphine compound which fully inhibits both thermal and ultraviolet fog without a noticeable reduction in photographic speed is within the narrow range of 0.1 to 0.2 ccs. of a 1% solution of the triphenylphosphine compound; in Example 3, the amount of the related triphenylarsine compound for producing the same optimum effect of inhibition of thermal and ultraviolet fog without noticeable reduction in photographic speed is in the range of 0.15 to 0.2 ccs. of a 1% solution; in Example 4, the amount of triphenylstibine compound required to produce the same effect is in the range of 0.2 to 0.3 ccs. of a 1% solution, and; in Example 5, the amount of triphenylbismuthine compound to produce a comparable effect as defined in the previous three examples is between 0.2 and 0.4 ccs. of a 1% solution. In using the tetraphenyl-distibine compound as a substitute for the triphenylstibine compound approximately the same weight of the tetraphenyl-distibine compound was found to be optimum as the triphenylstibine compound. Since the molecular weight of the tetraphenyl-distibine compound is approximately double that of the triphenylstibine compound, the conclusion drawn with respect to the effect of the stabilization reaction being directly proportional to the molecular weight of the compound in an entirely homologous series appears to be confirmed. In addition, the conclusion with respect to the effect of the amount of metal atom present in the compound on an atomic weight basis, said metal atom being that attached to the aryl substituent, also appears to be confirmed.

TABLE I

Name	Formula	M.P., ° C.	M.W.	Metal, g./mol.
Tetraphenyl germane.....	Ph ₄ Ge.....	233	380	72
Tetraphenyl tin.....	Ph ₄ Sn.....	229	427	119
Triphenyl (methyl) tin.....	Ph ₃ MeSn.....	61	365	119
Hexaphenyl ditin.....	Ph ₃ Sn.SnPh ₃	237	700	238
Trimethyl triphenyl ditin.....	Me ₃ Sn.SnPh ₃	106	514	238
Tetraphenyl lead.....	Ph ₄ Pb.....	228	515	207
Benzyltriphenyl lead.....	PhCH ₂ PbPh ₃	93	530	207
Triphenyl phosphine.....	Ph ₃ P.....	80	262	31
Triphenyl arsine.....	Ph ₃ As.....	60	306	75
Triphenylstibine.....	Ph ₃ Sb.....	50	353	122
Tetraphenyl-distibine.....	Ph ₂ Sb.SbPh ₂	122	552	244
Triphenylbismuthine.....	Ph ₃ Bi.....	78	440	209

In order that the N-vinyl compound, free radical source and fog eliminator may be most effectively brought into association intimately with one another it is found preferable to place them all in solution in a suitable vaporizable solvent, preferably in between about 500 and 1000 cc. of a mixture of organic ketones, alcohols or hydrocarbon solvents for the quantities previously specified. The three active ingredients in the mixture may be augmented by the addition of any other ingredient for specific benefits, e.g. U.V. absorbers may be added to increase the response to U.V. or plasticizers may be added to the solution, or other additions such as those described in the above patents may be made.

The solution may be applied to paper, cloth or other absorptive support, or up to about 100 parts by weight of a binder material may be dissolved in the above solution and then the composition may be laid down on a suitable inert substrate such as glass, or on a porous substrate such as subbed Mylar (polyethylene terephthalate).

After evaporation of the solvent a thin film either supported or self-supporting results in which the active ingredients are uniformly dispersed.

Suitable binders include the following which are merely given by way of example since many other binders could be used in the practice of this invention:

TABLE II

Binder:	Solvent
Cellulose acetate	30 methylene dichloride +70 acetone.
Cellulose nitrate	30 ethyl alcohol+ethyl ether.
Ethyl cellulose	30 acetone+40 toluene +30 methyl alcohol.
Polyethylene	30 toluene+10 acetone.
Polymethylmethacrylate ..	70 acetone+30 ethyl acetate.
Polystyrene	90 toluene+10 acetone.
Polyvinylacetate	40 methyl alcohol+40 acetone+20 toluene.
Polyvinylchloride	80 tetrahydrofuran+20 acetone.
Polyvinylidene chloride co-polymer (Saran)	80 tetrahydrofuran+20 acetone.

The relative proportion of the fog eliminator in the above described compositions must be maintained within the limits stated in order to accomplish the desired result. If the stated limiting value is exceeded the photosensitivity of the composition starts to decrease and if an excessive amount of the compounds is utilized, the photosensitivity of the composition is lost entirely. This reduction in photochemical activity starts to become noticeable at the upper limit of the fog eliminator listed above. If the amount of fog eliminator is increased by 50% over this maximum limit, the reduction in photochemical activity is such that the composition is virtually useless for the production of a visible image having a practicable density. While it is possible that the photochemical action proceeds unhindered even at these concentrations, the result is not a useful one. The combination of an N-vinyl compound such as N-vinyl carbazole and a halomethane such as carbon tetrabromide will produce an image under proper conditions on exposure to light between 3000 A. and 4400 A. with the peak of sensitivity in the range of 3500 A. and 4000 A. A convenient light source for the production of images on such systems is a G.E. Reflector type Sunlamp of 275 watts capacity. Depending on its age such a lamp will yield actinic energy for the photographic system in question in the range of 2 to 5 milliwatt per square centimeter per second at the image plane with the lamp being approximately 12" away from such image plane. Thus, an exposure of 1 second under such conditions will yield approximately 4 to 5 milliwatts per square centimeter if the lamp is new and about half this value after the lamp has been used for a few weeks. Under the conditions described, and utilizing the chemical systems described in this specification an exposure time of 2 seconds or more is considered normal and it is relatively easy to obtain an image by a variety of thermal development techniques without the development of background fog. However, even then, fog develops very slowly in the unexposed portions on storage so that a distinct brownish tinge in the background areas develop after about a month of such storage. For exposure times less than 2 seconds and in the range of fractions of a second somewhat more drastic thermal treatments are required to bring out an image and it appears that as a consequence of these more drastic thermal treatments the development of background fog on storage develops more rapidly than under normal storage. In both cases, a blanket re-exposure to the ultraviolet light source for extended periods of time also is a source of fog. The use of the metallo-organic compounds described in this specification not only eliminates the development of thermal fog in the initial development but also eliminates the development of storage fog and in addition stabilizes the films indefinitely to

lengthy exposures of a blanket nature involving ultraviolet light.

For exposure times of 2 seconds or more, thermal development may be completed by heating the ultraviolet exposed surface at temperatures between 90 and 120° C. for periods of time up to 60 seconds and generally thermal fog will not develop even if this time is extended to about twice this maximum period i.e. to 120 seconds. While oven or hot plate treatment may be utilized for the thermal development purpose a convenient method for achieving the same result is to treat the previously light exposed image to the radiation from a 250 watt infrared lamp of the reflector type whose glass envelope is comprised of red ruby glass and placed at a distance of about 6". Exposure to such a lamp will bring the temperature of the image into the desired range of 90 to 120° C. in a few seconds and about the same length of time of exposure to such a lamp is conveniently used as when an oven or a hot plate is utilized. Sometimes it is convenient to use a combination of these two energy sources. The exposed material may be inserted in an oven at 120° C., retained therein for about 1 minute and the thermal development finished by exposure to the infrared lamp for a few seconds only.

For light exposure times of less than 2 seconds using the levels of radiation defined in earlier paragraphs, thermal development under the conditions just described requires about 2 minutes. The time may be shortened by increasing the temperature levels to a range of 135 to 150° C. in the oven or by making the infrared lamp exposure for thermal development at a distance of 4" rather than 6" and also for times comparable to that used in the oven. As indicated, when these higher temperatures or longer times are utilized to bring out images which have been exposed for less than 2 seconds (or in the range of 4 to 10 milliwatts per square centimeter) and particularly for values substantially lower than this amount a notably tendency towards increased thermal fog, fogging on storage after thermal development, and sensitivity to fogging on subsequent exposure to ultraviolet light is developed at an increasing rate in view of the increased thermal treatment required.

The metallo-organic compounds described in this specification permit thermal or infrared development to be carried out with relative impunity in a temperature range of 135 to 150° C. even though the time of thermal development may be extended unduly in order to bring out images which have been obtained by light exposures very substantially less than the two seconds exposure indicated with the light source herein described. Under the conditions and concentrations described in this specification, thermal fog, fog on storage and protection against subsequent fogging by inadvertent blanket exposure to long periods of ultraviolet light are substantially eliminated.

In the examples which follow the standard exposure source was a 275 watt G.E. Reflector type Sunlamp utilized at a distance of 12" from the image plane. The standard thermal or infrared development step utilized a 250 watt reflector type infrared lamp whose envelope is comprised of red ruby glass at a distance of 4". Thermocouple measurements obtained by imbedding the head of the thermocouple directly in the film exposed under these conditions indicates that a temperature of 135 to 150° C. is reached in about 15 seconds and stabilizes in this temperature range substantially indefinitely.

The following examples will illustrate compositions which have been found to be effective in the practice of this invention.

Example 1

A photosensitive composition was prepared consisting of:

10 cc. of 10% polyvinylchloride in tetrahydrofuran
5 cc. of 25% N-vinyl carbazole in toluene
5 cc. of 25% carbon tetrabromide in benzene

The above solutions were mixed under a yellow safe light and while under the yellow safe light the resulting mixture was drawn down on a flat glass plate with a doctor blade developing a 0.003" of wet thickness. The freshly prepared slide was then allowed to stand in the dark until all the solvent has been dissipated by evaporation leaving the composition as a thin dry film of polyvinylchloride containing a solution of the mixture of carbon tetrabromide and N-vinyl carbazole. Approximately 10 minutes was required for complete drying.

Then the dried film was given an imagewise exposure for a time duration of 1 second to a G.E. 275 watt reflector type sunlamp at a distance of 12". On examination under the yellow safe light after the termination of such exposure it was evident that no visible image had been obtained. Thereafter the previously exposed plate was placed under a 250 watt ruby glass reflector type infrared lamp at a distance of 4". In about 45 to 60 seconds a strong black-brown image started to appear in those portions of the film which had been previously exposed to ultraviolet light. The background remained clear for about 15 seconds thereafter while the density of the image portions continued to build up, and then fogging started to develop and after a total elapsed time under the infrared lamp of 120 seconds the extent of fogging was quite severe to the point where the density of the background appeared to be at least 50% or more of that of the still retained image.

A fresh dried film prepared under the yellow safe light as before was treated in exactly the same manner as described in the previous paragraphs except that the exposure to ultraviolet light covered a time period of 0.1 second. Under these conditions the infrared development started to produce a brownish-black image after approximately 100 seconds of thermal treatment and did not appear to yield the full density in the previously exposed ultraviolet light areas until about 120 seconds. However, with the attainment of full density thermal fog in the unexposed portions was already well advanced. Though an image was readily discernible under these conditions the degree of background fog was such that the density of the background areas was at least 75% of the optical density of the image portions. This last plate was then given a blanket exposure to the ultraviolet lamp at a distance of 12" and within 2 minutes of such exposure fogging had proceeded to such an extent that the image practically disappeared.

Example 2

A photosensitive composition was prepared consisting of:

10 cc. of 10% polyvinylchloride in tetrahydrofuran
5 cc. of 25% N-vinyl carbazole in toluene
5 cc. of 25% carbon tetrabromide in benzene
0.15 cc. of 1% triphenylphosphine in benzene

The above composition was prepared in the same manner as in Example 1 and exposed under the ultraviolet light source for 0.1 second. A thermal treatment extending for 120 seconds was given the film utilizing a 4" distance from the infrared lamp as in Example 1. Under such treatment an image optical density of 1.22 was obtained with a background density of 0.04. The glass slide containing the exposed film was then cut in half. One half of the film thus produced was placed in a drawer for ageing purposes and the density difference between image and background again measured 30 days later. The optical density of the image was now 1.25 and the optical density of the background was 0.05. The other half of the plate was given a blanket exposure to the General Electric sunlamp at a distance of 12" for 60 minutes. After such exposure the optical density of the image was 1.37 and the density of the background was 0.08.

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Example 3

A photosensitive composition was prepared consisting of:

- 10 cc. of 10% polyvinylchloride in tetrahydrofuran
- 5 cc. of 25% N-vinyl carbazole in toluene
- 5 cc. of 25% tribromacetophenone in acetone
- 0.2 cc. of 1% triphenylarsine in benzene

The composition was prepared as a dry film from a 3 mil wet thickness as in the preceding examples and after drying was given the exposure and post exposure treatments as defined in Example 2. An image density in excess of 1.0 was achieved and after the various fogging and aging treatments background density was less than 0.1 and was again accompanied with a slight increase in image density.

Example 4

A photosensitive composition was prepared consisting of:

- 10 cc. of 10% polyvinylchloride in tetrahydrofuran
- 5 cc. of 25% N-vinyl carbazole in benzene
- 5 cc. of 25% tribromacetophenone in acetone
- 1 cc. of 20% diphenylamine in benzene
- 0.25 cc. of 1% triphenylstibine in benzene

The preparation and imagewise exposure of the composition were the same as in Example 2. Again the same stability towards thermal fog, ultraviolet fog and ageing was obtained with density differences between image and background in excess of 1.0. The primary difference in the result between Example 4 and the previous examples was the blue-black color of the image as compared with the brown-black color of the permanent image obtained in the previous examples.

Example 5

A photosensitive composition was prepared consisting of:

- 10 cc. of 10% polystyrene in benzene
- 5 cc. of 25% N-vinyl carbazole in benzene
- 5 cc. of 25% tribromacetamide in ethylether
- 0.35 cc. of 1% triphenylbismuthine in benzene

The composition given above was prepared and exposed as in Example 2. Again, a density difference between image and background of at least 1.0 was achieved immediately after the full thermal treatment and this density difference was expanded after the various fogging treatments recited in Example 2.

Example 6

A photosensitive composition was prepared consisting of:

- 10 cc. of 10% polyvinylchloride in tetrahydrofuran
- 5 cc. of 25% N-vinyl carbazole in benzene
- 5 cc. of 25% tribromacetophenone in acetone
- 1 cc. of 20% diphenylamine in benzene
- 0.20 cc. of 1% tetraphenyldistibine ($\text{Ph}_2\text{Sb.SbPh}_2$)

The results obtained on exposure, infrared treatment and fogging with the composition given in Example 6 are substantially identical with those obtained in Example 4.

Example 7

A photosensitive composition was prepared consisting of:

- 10 cc. of polyvinylchloride in tetrahydrofuran
- 5 cc. of 25% N-vinyl carbazole in toluene
- 5 cc. of 25% carbon tetrabromide in benzene
- 10 cc. of 1% triphenylstibine in benzene

Again, the composition defined immediately above was given the total exposure and thermal development as defined in Example 2. The optical density of the image obtained was 0.67 and the optical density of the background

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was 0.04 making a total density difference of 0.63. Substantially no change in optical density of the background was obtained on the various fogging treatments described in Example 2 and a very slight barely measurable increase in image density was obtained as the result of the ultraviolet fogging. This result indicates the potent effect of the metallo-organic compound as an eliminator of fog and development.

Example 8

A photosensitive composition was prepared consisting of:

- 500 cc. of 25% N-vinyl carbazole in benzene
- 500 cc. of tribromacetophenone in acetone
- 25 cc. of triphenylstibine in benzene

The composition as given immediately above was prepared under a yellow safe light as before in solution form. In this case, however, a 20# weight bond paper was inserted in the solution until soaked, removed from the solution and hung up in the darkroom until dry, requiring about 10 minutes for complete elimination of the solvent. The paper carrying the therein disposed photosensitive mixture was imagewise exposed as in Example 2. In the thermal development as defined in Example 2, it was noted that the image appeared to be fully developed in less than 60 seconds and no noticeable degree of fog was achieved by extending this thermal development to 120 seconds. After 120 seconds of thermal development the image density obtained was 2.35 and the background density 0.09.

Example 9

The composition of Example 8 was prepared under a yellow safe light as before in solution form. In this example, however, a sheet of 20# weight bond paper was first subbed to prevent penetration of the photosensitive solution by first soaking the sheet in a 10% solution of polyvinyl alcohol in water, then drying the sheet, and then calendering the dried sheet. The photosensitive solution was either doctor bladed or roll coated on the subbed bond paper and imagewise exposure and development of a visible image were effected as in Example 8.

Example 10

The same procedure of Example 9 was followed except that a dried gelatine surface was used instead of paper. The same results were obtained.

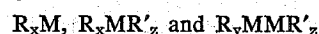
Having now described the invention in accordance with the patent statutes it is not intended that it be limited except as required by the appended claims.

I claim:

1. A normally colorless light-sensitive composition consisting essentially of at least one of each of the following constituents:

- (1) An N-vinyl compound
- (2) An organic halogen compound which decomposes to yield free radicals when subjected to a suitable dose of radiant energy

- (3) An anti-fogging agent selected from the group represented by a formula selected from the group consisting of



wherein R represents a radical selected from the group consisting of aryl and alkaryl, and R' represents a radical selected from the group consisting of alkyl, aryl, alkaryl and aralkyl and R and R' may each represent more than one kind of radical in any one compound, and wherein M represents an element selected from the group consisting of Ge, Sn, Pb, P, As, Sb and Bi and wherein x, y and z are integers from 1 to 4 such that the total number of R and R' satisfies the valence of M.

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2. The composition of claim 1 wherein the organic halogen compound is selected from the group consisting of normally solid compounds in which three halogen atoms are attached to a single terminal carbon atom.

3. The composition of claim 1 wherein the compound is represented by the formula $A-C-Br_3$ wherein A is selected from the group consisting of halogen, alkyl, haloalkyl, aryl and aroyl.

4. The composition of claim 1 wherein R is a phenyl and x is 3 and M is a trivalent element.

5. The composition of claim 1 wherein at least 3 of the radicals are phenyl and x is 4 and M is a tetravalent element.

6. The composition of claim 1 dispersed in a solid support.

7. The composition of claim 1 dispersed on a solid support.

8. The composition of claim 1 dispersed in a film-forming plastic base.

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9. The composition of claim 1 wherein for each 0.1 to 10 parts by weight of fog eliminating compound in the composition, there are between 10 and 200 parts by weight of N-vinyl compound and between 10 and 200 parts by weight of organic halogen free radical source.

10. The process which comprises preparing the composition of claim 1 supported as a thin layer, exposing said composition imagewise to radiation in the 3000 Angstrom to 4500 Angstrom range and developing the resulting image by means of heat.

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