

PATENT SPECIFICATION

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(54) VESICULAR IMAGING COMPOSITION, MATERIAL AND PROCESS

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a photographic vesicular imaging composition, material and process. In particular, it concerns an imaging composition and material containing a radiation-sensitive vesiculating agent which imagewise decomposes to form microscopic light-scattering vesicles of gas, usually within an appropriate binder. A spectral sensitizer may be used to extend the range of responsiveness.

Vesicular films are of considerable importance in information storage and retrieval, such as by microfilming, because vesicular images have very high resolution and are extremely stable in ambient light and normal use temperatures. One of the most common classes of vesiculating agents is diazonium salts which, upon exposure to activating radiation, release nitrogen gas. By an appropriate selection of the binder, the gas is retained within the material until development by heat causes expansion of the gas into light-scattering vesicles.

One of the more conspicuous problems of vesicular imaging has been the lack of a system which permits spectral sensitization of the vesiculating agent. Such lack is particularly noteworthy at a time when well-developed techniques are available for the spectral sensitization of photographic silver halide materials and even diazo-coupler dye materials are being spectrally sensitized. The result of such a lack is, of course, a limitation of the spectral response of the vesiculating material to that of the particular vesiculating agent used. The sensitivity of such agents is generally in the ultraviolet or near UV portions of the spectrum. UV sources are difficult to obtain, and furthermore interposition of any material which has a filtering effect on UV light reduces the sensitivity of such vesiculating agents to the point of rendering them less desirable for practical purposes. A filtering effect can result from the preparation of vesicular prints from negatives coated on polyethylene terephthalate film base due to the intensive absorption of light at certain short wavelengths by this film base material.

A clear and continuing need has existed for a vesicular imaging composition and material that is capable of being spectrally sensitized beyond the inherent sensitivity of the vesiculating agent.

It would also be desirable for a vesicular imaging composition and material to provide enhanced reprint contrast.

Advantageously, the vesiculating agent should be thermally stable over all useful temperature ranges.

Furthermore, it would be beneficial for the vesicular imaging composition and material to involve non-corrosive ingredients only.

The invention concerns a vesicular imaging composition, material and process utilizing a class of vesiculating agents that can be spectrally sensitized.

In accordance with the invention there is provided a vesicular imaging composition comprising: (I) a polymeric binder having sufficient gas impermeability to provide a latent image stability period as hereinafter defined for CO that is greater than one minute when coated in a material having a dried binder thickness of from 10 to 15 microns; and (II) admixed with the binder, a radiation-decomposable vesiculating agent capable of generating CO upon imagewise exposure, the vesiculating agent being a cyclopropanone having a λ_{\max} in ethanol no greater than 400 nm in the spectral range of from 250 to 650 nm.

With such vesiculating agents, increased spectral sensitivity can be achieved by the incorporation of a spectral sensitizing compound having a λ_{\max} in methanol which is less than 450 nm.

The invention also provides a vesicular imaging material comprising a support having coated thereon a composition of the invention.

The process of the invention comprises the steps of imagewise exposing the aforesaid material to activating radiation to provide a developable latent image in the material, and developing the resulting image by heating the material to a temperature and for a time sufficient to force CO bubbles formed by the photodecomposition of the vesiculating agent to expand to form a visible image.

The invention provides vesicular imaging compositions and imaging materials coated in a film format such as on a suitable support. However, it will be appreciated that the invention also includes any imaging material utilizing the compositions hereinafter described. For example, certain polymeric binders by reason of their self-sustaining nature may render the need for a support unnecessary.

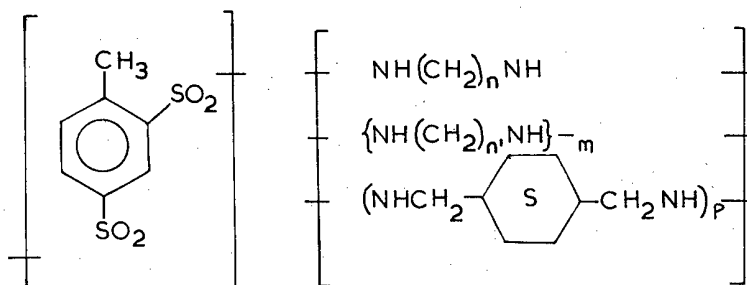
Thus, the preferred material of the present invention comprises a support, if used, and coated on at least one surface of the support, a layer comprising a suitable binder and a cyclopropanone vesiculating agent. Any suitable photographic support may be used in the practice of this invention. Typical supports include transparent supports, such as film supports and glass supports as well as opaque supports, such as metal and photographic paper supports. The support may be either rigid or flexible. The most common photographic supports for most applications are paper or film supports, such as poly(ethylene terephthalate) film. Suitable exemplary supports are disclosed in *Product Licensing Index*, Vol. 92, December 1971, Publication 9232, at page 108, published by Industrial Opportunities Ltd, Homewell, Havant Hampshire, PO9 1EF United Kingdom. The support may incorporate one or more subbing layers for the purpose of altering its surface properties so as to enhance the adhesion of the radiation-sensitive coating to the support. A typical example of a subbing material is the terpolymer of vinylidene chloride, acrylonitrile, and vinyl chloride.

With regard to the matrix or binder of the material, although most of the embodiments hereinafter described use a polysulphonamide binder, other binders compatible with the cyclopropanone vesiculating agent and its solvent may also be used. For example, the binder may be selected from poly(vinyl chloride), poly(vinylidene chloride), and polystyrene; copolymers obtained by copolymerizing acrylonitrile with vinyl chloride, styrene, vinylidene chlorofluoride, or 1,1-difluoroethylene; copolymers obtained by copolymerizing vinyl chloride with methyl acrylate, acrylic acid, diethyl maleate, or vinyl acetate; and, copolymers obtained by copolymerizing vinylidene chloride with vinyl chloride, vinyl acetate, vinyl alcohol, ethyl acrylate, or acrylonitrile. Examples of the homo- or co-polymerization of vinylidene chloride are described in U.S. Patent No. 3,032,414. Other binders include α -chloroacrylonitrile preferably mixed with other copolymers such as those disclosed in U.S. Patent No. 3,620,743, and Bisphenol A/epichlorohydrin copolymer. As used herein, "Bisphenol A" means 4,4'-isopropylidene diphenol, sometimes known as 2,2-(p-hydroxyphenyl)propane.

With regard to the polysulphonamide binders, suitable compositions and a method of preparing them are described in *Research Disclosure*, Vol. 131, Publication No. 13107, March 1975, published by Industrial Opportunities Ltd. Generally, such polymeric binders have the group $>\text{N}-\text{SO}_2-$ as a portion of the polymer backbone or as a pendant moiety so as to possess the proper permeability constant for vesicular imaging and also to produce enhanced responsiveness in vesicular photographic materials. Thus it has been found that any sulphonamide polymer of this type is suitable, provided that the wavelength of maximum absorption of the binder, λ_{\max} , is no greater than about 350 nm in the spectral range

of 200 to 750 nm and is preferably lower than 300 nm. It has been determined that higher values of λ_{\max} tend to produce coloured binders which interfere with the absorption of light that is necessary to decompose the vesiculating agent. Particularly useful classes of such polymers include polymers containing toluene-2,4-disulphonamide units and those containing N-(vinylphenyl)-sulphonamide units. The binders of this class may be homopolymers, copolymers, or physical mixtures of the same. Whether the polymer is an addition polymer or a condensation polymer, a certain portion of the polymer should be recurring sulphonamide groups so that the weight percent of sulphur is at least about 4%.

Another useful class of polysulphonamide binders includes binders having the general formula:



where n and n' are the same or different and are each a positive integer from 2 to 12; m is 0 or 1; and p is 0 when m is 1, and is 1 when m is 0.

With respect to the above-described binders, these satisfy the gas impermeability requirement for vesiculating materials wherein the imaging layer must be sufficiently impermeable to the decomposition gas formed upon exposure to retain it long enough to form the imaging vesicles upon heating i.e. for greater than one minute. A conventional method for describing such gas impermeability has been to use the above-noted permeability constant described in U.S. Patent No. 3,032,414. The permeability constant has been required to fall within the range of from 1×10^{-11} to 1×10^{-15} .

However, the gas permeability constant of a binder material is relatively difficult to determine. Therefore, an alternative procedure is proposed to determine the suitability of a binder material for forming a vesicular image with a particular vesiculating agent, i.e., determining the latent image stability period of the binder material. As used in the specification and claims, the "latent image stability period" is the length of time required for the latent vesicles of gas (in this instance carbon monoxide) generated by the vesiculating agent on exposure to diffuse out of the imaging layer at 22°C until no image with a density greater than 0.2 is developable.

The latent image stability period of candidate binder material is determined by the following procedure:

(a) A material is prepared comprising a support bearing a vesiculating layer having a dry thickness of from 10 to 15 microns as hereinafter described and cut into test strips.

(b) The test strips are exposed for 36 seconds at ambient temperature, through a carbon step wedge to an undoped mercury arc lamp at a distance of 7.6 centimeters.

(c) The exposed test strips are stored at 22°C for various periods of time, and then

(d) developed by contacting with an aluminium block at 150°C for 2 seconds. The maximum specular density of each developed strip is ascertained.

The storage time necessary to produce no developable image of a density greater than 0.2 is the latent image stability period. It has been found that materials which produce satisfactory vesicular images are those in which the latent image stability period of the binder for CO is substantially greater than one minute when coated in a material having a dried binder thickness of from 10 to 15 microns. Highly preferred are those binders in which the gas impermeability for CO, under the test conditions noted, is such that the latent image stability period is equal to or greater than about 5 minutes. Specifically, it has been found that, using the above-described test, the latent image stability period for CO in poly(ethylene - co - 1,4 - cyclohexylenedimethylene - 1 - methyl - 2,4 - benzenedisulphonamide), one of the preferred binders of the element of this invention, is 44 minutes. For Bisphenol

A/epichlorohydrin, it is about 9 minutes. This compares with an essentially zero latent image stability period that was found when the same test was run using cellulose acetate butyrate, a polymer unsuited for vesicular imaging.

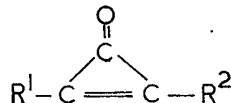
The materials used to test the latent image stability period were prepared as follows:

Polymer solutions were prepared by separately dissolving 1.470 gm of cellulose acetate butyrate, Bisphenol A/epichlorohydrin copolymer "epanol resin 55-B-40" sold by Shell Chemical Corp., and poly(ethylene - co - 1,4 - cyclohexylene - dimethylene - 1 - methyl - 2,4 - benzenedisulphonamide) in 9.900 gm of solvent. The solvent was composed of equal weights of acetone and 2-methoxyethanol. In each case a brilliant clear solution resulted by stirring at room temperature. An amount of 0.163 gm of 1 - phenyl - 2 - anisyl - cyclopropenone was added as a vesiculating agent to each solution. A clear solution resulted by stirring in each case. The polymer solutions were each coated using a 7 mil doctor blade on clear poly(ethyleneterephthalate) support. The coatings were then each dried on the coating block for 5 minutes at 24°C, 5 minutes at 43°C and by flash drying for 10 seconds at 150°C on a heated aluminium drying block. The photographic materials formed as described were dry except for traces of residual solvent, and were about 10 to 13 microns thick. The dry laydown was 12 to 15 g per square metre.

It will be further appreciated that other factors can alter slightly the actual numerical values of the stability period. Included here, at least for polymers having polar sites, is the amount of residual solvent present in the polymer. Longer latent image stability periods will result if the dried binder thickness is greater.

With respect to the vesiculating agent, it has been found that cyclopropenones comprise a class of agents which provide outstanding vesiculating characteristics, including improved thermal stability and the ability to be spectrally sensitized. To avoid the formation of colored cyclopropenones that effect the background of the image, λ_{\max} of such cyclopropenones, measured in ethanol between the spectral range of 250 to 650 nm, should be no greater than 400 nm, where λ_{\max} is defined to mean the wavelength of maximum absorption of the compound.

Highly preferred are the vesiculating agents having the formula:



wherein:

R^1 and R^2 are the same or different and are each a substituted or unsubstituted aryl radical having from 6 to 10 carbon atoms in the aromatic ring, for example, phenyl and naphthyl; or an aralkenyl radical having from 6 to 10 carbon atoms in the aryl portion and from 1 to 5 carbon atoms in the alkenyl portion, for example, 2,2-diphenylvinyl, 2-phenylvinyl, and 2-naphthylvinyl;

the substituents of each of the substituted aryl radicals being one or more radicals, present in any position on the aryl ring, selected from:

1) an alkyl or alkoxy radical containing from 1 to 5 carbon atoms, for example, methyl, ethyl, propyl, iso-propyl, butyl, methoxy, ethoxy, propoxy or butoxy;

2) a nitro radical;

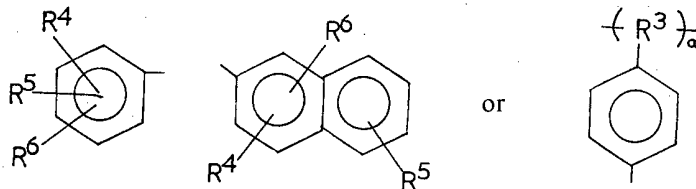
3) an aryloxy radical containing from 6 to 10 carbon atoms, for example phenoxy or naphthoxy;

4) a halogen atom, for example chlorine or fluorine; and

5) a polymer to which the aryl radical is attached as a dependent moiety, the polymer having at least one repeating unit which is a lower alkylene radical containing from 1 to 5 carbon atoms.

The polymer of substituent 5) may be a homopolymer or a copolymer having at least one repeating unit having the formula $(-\text{R}^3-)_a$ wherein R^3 is a lower alkylene radical containing from 1 to 5 carbon atoms, for example ethylene or propylene, and "a" is at least a portion of the number of repeating units in a given polymer chain.

Thus, R^1 and R^2 may each be any one of the following radicals:



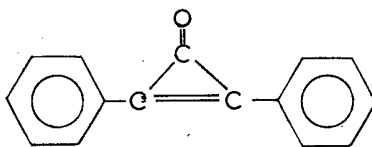
where R^4 , R^5 , and R^6 are the same or different and are any of the substituents defined above as 1), 2), 3), or 4 and R^3 is the repeating unit defined above as 5).

Preferably, at least one of R^1 and R^2 is a bi-substituted aryl radical.

The following representative cyclopropenones are useful vesiculating agents according to the invention. The λ_{\max} for these agents was determined by measuring ultraviolet absorption peaks for each cyclopropenone in a Beckman model DB spectrophotometer, after dissolving the polymer in spectrographic grade ethanol, and by visually examining the cyclopropenone coating to ascertain that no significant absorption occurs in the visible spectrum, i.e., in the range 400 nm to 750 nm. The 400 nm limit on the value of λ_{\max} for the cyclopropenones is preferred to avoid undue coloration in the background.

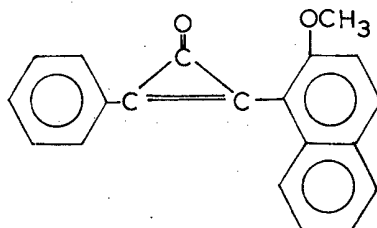
The units set forth for cyclopropenone No. 8 are recurring units of the polymer.

Cyclopropene No. 1



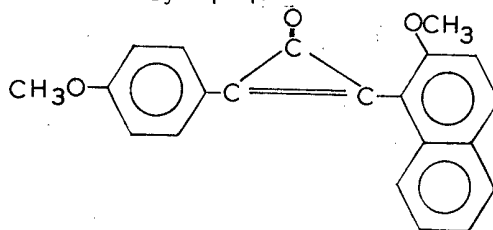
2,3-diphenylcyclopropenone
 $\lambda_{\max}=300$

Cyclopropenone No. 2



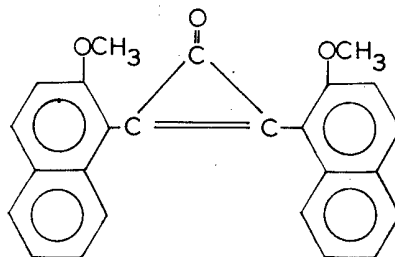
2-(2-methoxynaphthyl)-3-phenylcyclopropenone
 $\lambda_{\max}=371$

Cyclopropenone No. 3



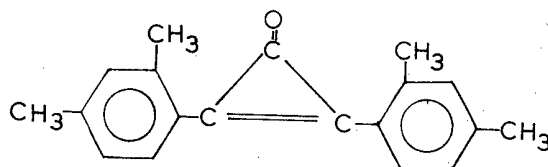
2-(2-methoxynaphthyl)-3-(4-methoxyphenyl)cyclopropenone
 $\lambda_{\max}=372$

Cyclopropenone No. 4



2,3-bis(2-methoxynaphthyl)cyclopropenone
 $\lambda_{\max}=390$

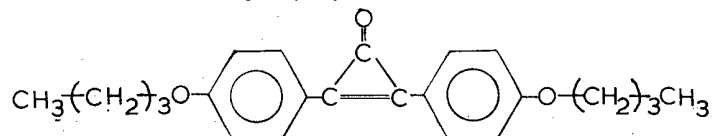
Cyclopropenone No. 5



2,3-bis(2,4-dimethylphenyl)cyclopropenone
 $\lambda_{\max}=325$

5

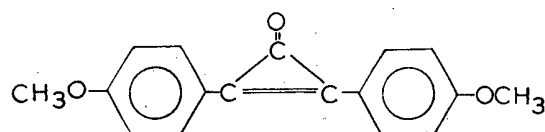
Cyclopropenone No. 6



2,3-bis(4-*n*-butoxyphenyl)cyclopropenone
 $\lambda_{\max}=328$

5

Cyclopropenone No. 7

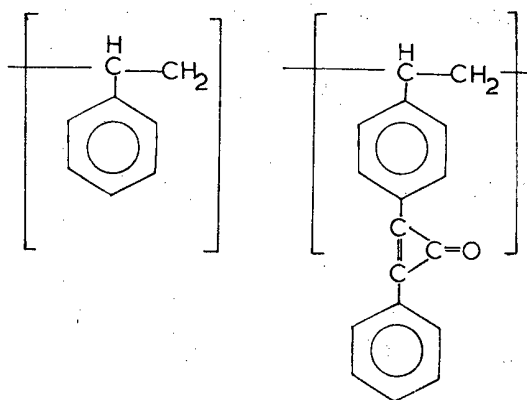


2,3-bis(4-methoxyphenyl)cyclopropenone
 $\lambda_{\max}=323$

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Cyclopropenone No. 8

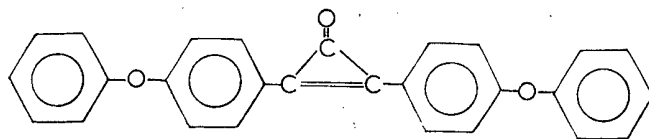


poly[styrene-co-4-(3-phenyl-2-cyclopropene-1-one-2-yl)styrene]
 $\lambda_{\max}=305$

15

15

Cyclopropenone No. 9

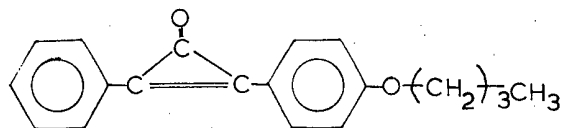


2,3-bis(4-phenoxyphenyl)cyclopropenone
 $\lambda_{\max}=326$

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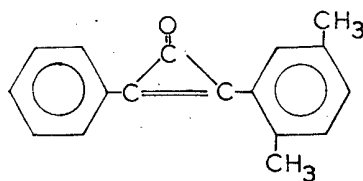
Cyclopropenone No. 10

2-(4-*n*-butoxyphenyl)-3-phenylcyclopropenone
 $\lambda_{\max}=318$

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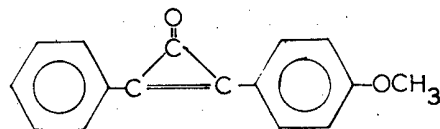
Cyclopropenone No. 11

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2-(2,5-dimethylphenyl)-3-phenylcyclopropenone
 $\lambda_{\max}=302$

Cyclopropenone No. 12

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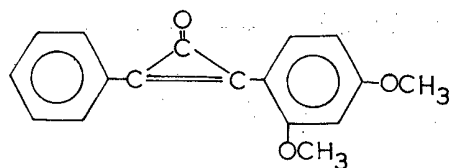


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2-(4-methoxyphenyl)-3-phenylcyclopropenone
 $\lambda_{\max}=313$

Cyclopropenone No. 13

15

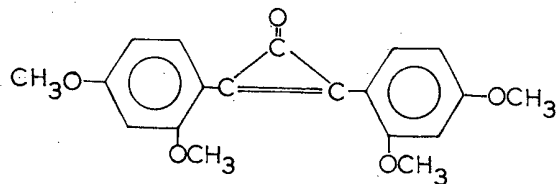


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2-(2,4-dimethoxyphenyl)-3-phenylcyclopropenone
 $\lambda_{\max}=342$

Cyclopropenone No. 14

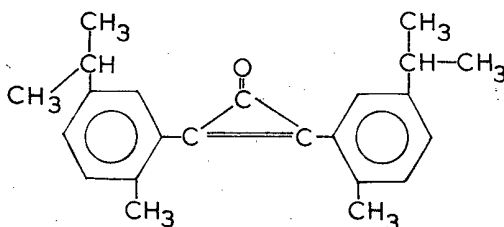
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2,3-bis(2,4-dimethoxyphenyl)cyclopropenone
 $\lambda_{\max}=350$

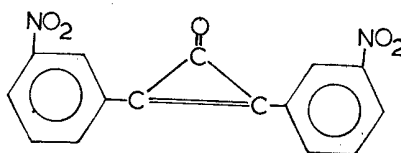
Cyclopropenone No. 15

2,3-bis(2-methyl-5-isopropylphenyl)cyclopropenone
 $\lambda_{\max}=300$

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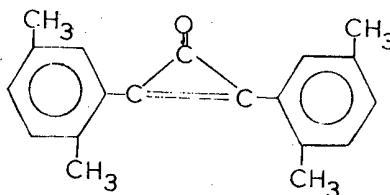
Cyclopropenone No. 16

5

2,3-bis(3-nitrophenyl)cyclopropenone
 $\lambda_{\max}=297$

Cyclopropenone No. 17

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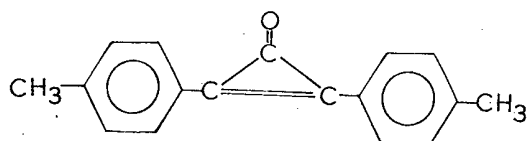


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2,3-bis(2,5-dimethylphenyl)cyclopropenone
 $\lambda_{\max}=325$

Cyclopropenone No. 18

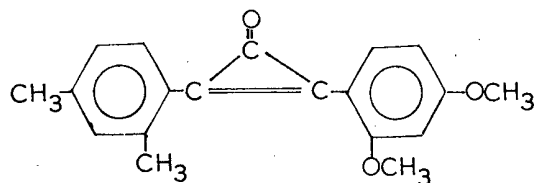
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2,3-bis(4-methylphenyl)cyclopropenone
 $\lambda_{\max}=310$

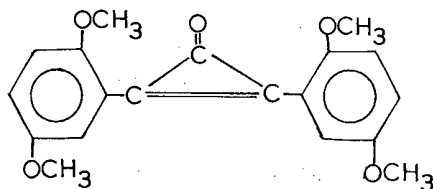
Cyclopropenone No. 19

2-(2,4-dimethoxyphenyl)-3-(2,4-dimethylphenyl)cyclopropenone
 $\lambda_{\max}=337$

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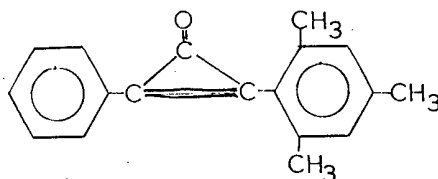
Cyclopropenone No. 20

2,3-bis(2,5-dimethoxyphenyl)cyclopropenone
 $\lambda_{\max}=380$

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Cyclopropenone No. 21

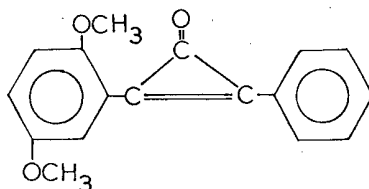
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2-(2,4,6-trimethylphenyl)-3-phenylcyclopropenone
 $\lambda_{\max}=285$

Cyclopropenone No. 22

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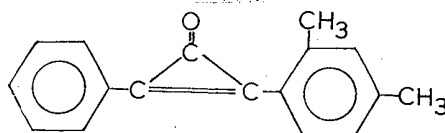
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2-phenyl-3-(2,5-dimethoxyphenyl)cyclopropenone
 $\lambda_{\max}=366$

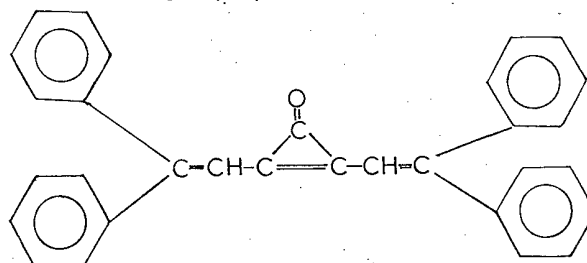
Cyclopropenone No. 23

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2-phenyl-3-(2,4-dimethylphenyl)cyclopropenone
 $\lambda_{\max}=310$

Cyclopropenone No. 24

2,3-bis(2,2-diphenylvinyl)cyclopropenone
 $\lambda_{\max}=374$

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The above cyclopropenones may be prepared by known processes, of which the following preparation of Cyclopropenone No. 2 is illustrative only:

A mixture of 14.0 g (0.11 mole) of anhydrous aluminium chloride and 17.8 g (0.10 mole) of tetrachlorocyclopropene in 200 ml of 1,2 - dichloroethane is stirred at room temperature for one hour. The mixture is cooled to 0°C and treated with 7.8 g (0.10 mole) of benzene, maintaining the temperature between 0° and 5°C. Upon completion of the addition, the reaction mixture is warmed slowly to 50°C, re-cooled to -25°C, and treated with a solution of 15.8 g (0.10 mole) of 2 - methoxynaphthalene in 1,2 - dichloroethane, maintaining the temperature between -25 and -20°C. Upon completion of the addition, the reaction mixture is allowed to warm to room temperature, and treated with ice and ice-water. The organic layer is separated, stripped *in vacuo*, and the resulting residue recrystallized from methanol to furnish 17.5 g of product, 2 - (2 - methoxynaphthyl) - 3 - phenylcyclopropenone.

The preparation of cyclopropenone No. 8 can be achieved as follows:

Trichlorocyclopropenium chloridoaluminate was prepared by reacting equimolar amounts of tetrachlorocyclopropene and aluminium chloride in 1,2 - dichloroethane solution. A convenient mole proportion of trichlorocyclopropenium chloridoaluminate suspended in the 1,2 - dichloroethane was cooled to 0°C. One equivalent weight of benzene was added slowly to the suspension while the mixture was stirred. The mixture was allowed to warm up slowly from 0°C to ambient temperature to complete the reaction. A five percent solution of the polystyrene was prepared in a second reaction vessel by dissolving two mole equivalents based on styrene monomer in 1,2 - dichloroethane. One mole equivalent of the cyclopropenium ion, in suspension, was added slowly to the polystyrene solution. The resulting mixture was stirred at room temperature for one hour to complete the reaction.

The complexes resulting from the reaction were decomposed by adding a small amount of methanol to the 1,2 - dichloroethane suspension followed by excess water at 5°C. The resulting emulsion was poured into an excess amount of methanol and the suspension agitated at high speed in a Waring Blender. The product remained suspended in the methanol while the impurities dissolved in the methanol. The fibrous solid product was obtained by filtering the suspension and washing the solid with methanol. The white coloured product was dried under vacuum to remove the volatiles.

One advantage of the cyclopropenone vesiculating agent used in the invention is that it can be spectrally sensitized by the addition of certain compounds. "Spectral sensitization" as used herein means the process by which the spectral sensitivity of the material is extended beyond the region of the electromagnetic spectrum to which the vesiculating agent is itself responsive. Preferred spectral sensitizers are separate compounds, having the above capability, which are not an integral moiety of the vesiculating agent prior to use.

As used in this application, the "limit of spectral sensitivity" means the maximum wavelength of exposure that would still produce in the element a density above fog, this wavelength sometimes being called the "cut-off absorbance".

Particularly useful spectral sensitizers with the vesiculating agents described above are those which have a λ_{\max} in methanol which is less than 450 nm. While this limitation is not completely understood from a mechanistic point of view, it is likely that λ_{\max} greater than 450 nm tends to interfere with the energy transfer mechanism which permits the sensitization of the cyclopropenone.

In selecting a spectral sensitizer, it has been found that a convenient test to determine which will perform satisfactorily is as follows:

Test Procedure

An amount of 0.047 moles of the candidate is co-dissolved with a disulphonamide polymer, such as 3/4 g of poly(ethylene - co - 1,4 - cyclohexylenedimethylene - 1 - methyl - 2,4 - benzene disulphonamide) with an image-generating amount of any cyclopropenone disclosed herein in a suitable solvent, such as in 1.25 g acetone, 2.75 g methoxyethanol and 0.25 g N,N - dimethylformamide. Only that amount of cyclopropenone need be included which is sufficient to generate an image upon exposure to activating radiation. The composition is coated on a suitable support, such as poly(ethylene terephthalate) and dried to remove all but residual solvent, and the dried coating is exposed to a wedge spectrograph incorporating a B & L half meter monochrometer and a 900 watt Xenon arc. The spectral response of the composition as developed after exposure to the wedge spectrograph is examined at wavelengths longer than the limit of spectral sensitivity of the cyclopropenone but still in the absorbance region

of the sensitizer candidate which preferably has a λ_{\max} in methanol of less than 450 nm. If an image response is obtained at these wavelengths, then spectral sensitization has occurred.

Following the above test, it has been found that 2 - benzoylmethylene - 3 - methyl-naphtho - (2,1 - a)thiazoline (hereinafter "BNTZ"), 3 - carboxymethyl - 5 - (3 - ethylbenzothiazolinyldene)rhodanine, anhydro - 3,3' - disulphopropyl - 5 - methoxythiacyanone hydroxide, and 2 - [bis(2 - furoyl)methylene] - 1 - methyl-naphtho[1,2 - d]thiazoline particularly demonstrate a high degree of extended spectral sensitivity. Each of the above compounds has a λ_{\max} in methanol which is less than about 450 nm. For example, λ_{\max} of BNTZ is 410 nm. Although λ_{\max} of anhydro - 3,3' - disulphopropyl - 5 - methoxythiacyanine hydroxide is 437 nm, it also absorbs beyond 450 nm. Combinations of spectral sensitizers can be used if desired.

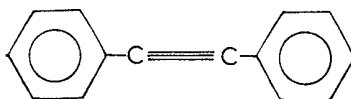
Because of the above-described spectral sensitizers, the spectral sensitivity of the preferred cyclopropenone vesiculators can be extended to almost 500 nm.

A useful embodiment of the invention is a vesicular imaging material prepared from the above cyclopropenone vesiculating agents by coating a layer of a solution comprising the binder, vesiculating agent and other desired addenda such as the spectral sensitizer, using coating techniques known in the photographic art. If the binder is not self-supporting, the coating is applied to a support. The support is preferably treated prior to coating with a conventional subbing material such as a terpolymer of vinylidene chloride, acrylonitrile and vinyl chloride. Suitable solvents for the coating include mixtures of ethanol, methanol, acetone, methoxethanol, dimethylformamide, cyclohexanone, chloroform, dichloromethane and trichloroethane. These solvents are also suitable for the spectral sensitizers described above.

The binder concentration in the solution may be between 2 and 20% by weight. The concentration of cyclopropenone is preferably between 10 and 25% of the weight of the binder, and the concentration of sensitizer between 0.05 and 1.5% of the binder weight. Total solids content of the element is preferably between 2.0 and 6.5 g/m² of coating. Typically, the solution is coated onto the support, if used, by such means as whirler coating, brushing, doctor-blade coating or hopper coating. Thereafter, the solvent is evaporated. Other exemplary coating procedures are set forth in the *Product Licensing Index*, Vol. 92, December 1971, publication 9232, at p. 109, published by Industrial Opportunities Ltd., as noted above, and include melts which are extruded to form the film.

Coating aids may be incorporated into the coating composition to facilitate coating as disclosed on p 108 of the above *Product Licensing Index* publication. It is also possible to incorporate antistatic layers and/or matting agents as described in the above *Product Licensing Index* publication. Plasticizers may be incorporated to modify the coatability or flexibility of the binder, if desired. Increased speed may be achieved by certain conventional addenda, at least some of which function as prenucleating agents which form sites for the gas bubbles, insuring a finer grain pattern. Examples of such prenucleating agents include waxes such as are taught in U.S. Patent No. 3,355,295. Finely divided pigment having an index of refraction approximately equal to that of the binder also increases the speed, as does exposure to high humidity.

The prepared imaging material according to the invention may then be imagewise exposed to ultraviolet light or visible light containing a strong ultraviolet component, such as is obtained from mercury arc lamps to provide a developable latent image. Such exposure is believed to cause the cyclopropenone to decompose into



and carbon monoxide. Development is then achieved by heating the exposed material for a time and at a temperature sufficient to expand the CO gas within the exposed portion into vesicles. When the temperature of development is between 100°C and 150°C, a few seconds of heating suffices.

If desired, the unexposed portion of the material thereafter can be conventionally flash-exposed and stored at a temperature and for a time sufficient to allow the predominant amount of the gas generated by said flash exposure to diffuse out of the material. Typically storage can be for several hours at a temperature below about 45°C.

The following examples further illustrate the invention.

Example 1

5 An amount of 0.75 g of poly(ethylene - co - 1,4 - cyclohexylenedimethylene -
1 - methyl - 2,4 - benzene disulphonamide) binder, in which the ethylene and 1,4 -
cyclohexylene - dimethylene moieties were present on a 50/50 mole percent basis, 5
was dissolved in 4.5 g of acetone/methoxyethanol mixed 50/50 by volume. The
polymer had an inherent viscosity of 0.42 decilitres per gram in dimethylformamide
10 at 25°C and a glass transition temperature (T_g) of 142°C. A clear solution was
obtained by stirring and gentle heating. Two hundred milligrams of 2,3 -
diphenylcyclopropanone (λ_{\max} 300 nm) were added as a light-sensitive vesiculating 10
agent. The clear lacquer solution was coated at 40°C onto a 100 μ m
poly(ethyleneterephthalate) film support at a wet thickness of 600 microns and
dried at 57°C to remove all but residual solvent.

15 A sample of the above material was exposed for 8 seconds to a 125 Watt
undoped mercury arc lamp spaced about three inches (7.6 cm) from the film 15
through a carbon wedge of 0.15 log E steps to provide a developable latent image in
the material. The latent image was developed by heating the material on a heated
block for three seconds at 128°C. An image was obtained that had a maximum
specular density of 1.70.

Example 1A

20 A sample of the material prepared as in Example 1 was nucleated by exposure
to air at 38°C, 94% relative humidity for 10 minutes after which it was exposed and
processed as described for Example 1. The film speed measured at D=1.0 after
exposure to high humidity, was increased by 0.45 log E. Thus, the photographic 20
material as prepared in this example is spontaneously nucleated by exposure to
high humidity. 25

Example 2

30 As an illustration of the "Test Procedure" described above, an amount of
three quarters of a gram of poly(ethylene - co - 1,4 - cyclohexylenedimethylene -
1 - methyl - 2,4 - benzene disulphonamide), as described in Example 1, was 30
dissolved in a mixture of 1.25 g acetone, 2.75 g methoxyethanol and 0.25 g N,N -
dimethylformamide. A clear solution was obtained by heating gently (~30°C) and
stirring. Two hundred milligrams of 2,3 - diphenylcyclopropanone was added as a
light-sensitive vesiculating agent and fifteen milligrams of the spectral sensitizer
35 BNTZ, λ_{\max} =410 nm, was added for spectral sensitizing. 35

40 A clear lacquer solution was obtained which was coated on poly(ethylene
terephthalate) as described in Example 1. The coating, exposed on a wedge
spectrograph, showed a sensitivity range extending to 480 nm as shown by curve 10
in Fig. 1, compared to only about 375 for the same material but without the spectral
sensitizer, curve 12 in Fig. 1. Thus, there was demonstrated a spectral response at 40
410 nm that could only come from the sensitizer. Exposure of the material 40
imagewise and development as described in Example 1 gave an image which had a
maximum specular density of 2.10.

Example 3

45 An amount of three-quarters of a gram of poly(ethylene - co - 1,4 -
cyclohexylenedimethylene - 1 - methyl - 2,4 - benzene disulphonamide), as
described in Example 1, was dissolved in a mixture of 2.75 g of methoxyethanol,
1.60 g of N,N - dimethylformamide and 1.25 g of acetone. A clear solution was
obtained by gentle heating and stirring at 30°C. Two hundred milligrams of 2,3 -
50 diphenylcyclopropanone was added as a light-sensitive vesiculating agent, along
with 15 mg of 3 - carboxymethyl - 5 - (3 - ethylbenzothiazolinyldene)rhodanine
having λ_{\max} =425 nm, added as a spectral sensitizer. 50

55 A clear lacquer solution was obtained which was coated on
poly(ethyleneterephthalate) support as described in Example 1. The coating
exposed on a wedge spectrograph showed a sensitivity range extended to 480 nm. 55
Again, spectral sensitivity in the terms of the "Test Procedure" was demonstrated.
Exposure of the material imagewise and development as described in Example 1
gave an image which had a maximum specular density of 2.10.

Example 4

5 An amount of three-quarters of a gram of poly(ethylene - co - 1,4 - cyclohexylenedimethylene - 1 - methyl - 2,4 - benzene disulphonamide) described in Example 1 was dissolved in 2.25 g of acetone and 2.25 g methoxyethanol. A clear solution resulted from gentle heating and stirring. Thirtyfive milligrams of 2 - (2 - methoxynaphthyl) - 3 - phenylcyclopropenone was next dissolved in the polymer solution. 5

10 A clear lacquer solution was obtained by dissolving the vesiculator in the polymer which was coated on a poly(ethyleneterephthalate) support, as described in Example 1. The vesicular material was exposed and processed as described in Example 1. An image was obtained that had a D_{\max} specular density of 2.10. 10

Example 5

15 An amount of three-quarters of a gram of poly(ethylene - co - 1,4 - cyclohexylenedimethylene - 1 - methyl - 2,4 - benzene disulphonamide) as described in Example 1 were dissolved in 2.5 g of acetone and 2.25 g of methoxyethanol. A clear solution resulted. Thirty-five milligrams of the cyclopropenone of Example 4 was next dissolved in the polymer solution; along with 14 milligrams of anhydro - 3,3' - disulphopropyl - 5 - methoxythiacyanine hydroxide, $\lambda_{\max}=380$ nm, as the spectral sensitizer. 15

20 A clear lacquer solution was obtained which was coated on poly(ethylene terephthalate) support as described in Example 1. The coating, exposed on a wedge spectrograph, showed the sensitivity range extended to 480 nm, curve 20 of Fig. 2, compared to the value of about 425 nm, curve 22 of Fig. 2, achieved for the same element but without this spectral sensitizer. Enhanced spectral response, due to the sensitizer, is evident at 475 nm, a wavelength considerably longer than the limit of spectral sensitivity demonstrated by the cyclopropenone. Imagewise exposure of the material and processing as described in Example 1 gave an image which had a maximum specular density of 2.10. 20 25

Example 6

30 An amount of three-quarters of a gram of poly(ethylene - co - 1,4 - cyclohexylenedimethylene - 1 - methyl - 2,4 - benzene disulphonamide) were dissolved in 2.25 g of acetone and 2.25 g of methoxyethanol. A clear solution resulted. Thirty-eight milligrams of vesiculating agent 2,3 - bis(2 - methoxynaphthyl cyclopropenone) were next dissolved in the polymer solution. 30

35 A clear lacquer solution was obtained which was coated on poly(ethyleneterephthalate) support as described in Example 1. The vesicular material was exposed and processed as described in Example 1. An image was obtained that had a maximum specular density of 2.15. 35

Example 7

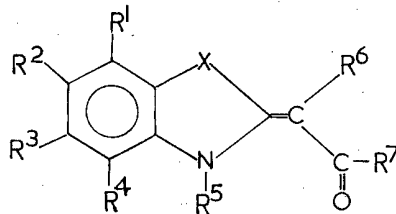
40 An amount of three-quarters of a gram of poly(oxy - 1,4 - phenylene dimethylmethylen - 1,4 - phenylene, oxy - 2 - hydroxytrimethylene), a Bisphenol A/epichlorohydrin copolymer, was dissolved as the binder in 2.25 g of acetone and 2.25 g of methoxyethanol. A clear solution was obtained by gently heating and stirring at 30°C. An amount of three hundred milligrams of the vesiculating agent of Example 1 was added as a light-sensitive vesiculating agent along with 18 milligrams of the spectral sensitizer of Example 2. 40 45

50 A clear lacquer solution was obtained which was coated on a poly(ethyleneterephthalate) support as described in Example 1. The coating was exposed on a wedge spectrograph which showed an extended sensitivity range to 480 nm. Imagewise exposure of the material and processing as described in Example 1 gave an image which had a maximum specular density of 2.10. 50

55 Our co-pending Application No. 4241/77 Serial No. 1,578,662 describes and claims a photosensitive composition comprising an unsaturated vesiculating agent and, as a sensitizer, a 3-substituted coumarin compound having an absorptive maximum of from 250 to 550 nm. It also describes and claims a vesicular material comprising a support coated with a layer of a heat-deformable, gas-impermeable polymeric binder containing an unsaturated vesiculating agent and a 3 - substituted coumarin compound having an absorptive maximum of from 250 to 550 nm, together with a method of forming a vesicular image which method comprises imagewise exposing the vesicular material to actinic radiation and heating the material sufficiently to allow the gas liberated by the vesiculating agent to expand within the polymeric binder. 55 60

We make no claim to the invention claimed in Application No. 4241/77 (Serial No. 1578662).

Our co-pending Application No. 16448/77 (Serial No. 1584741) describes and claims a photosensitive composition comprising an unsaturated vesiculating agent and a sensitizing amount of a sensitizer having an absorptive maximum at from 340 to 460 nm and having the following formula:



wherein X is a sulphur or a selenium atom; R¹, R², R³ and R⁴ independently represent hydrogen, a lower alkoxy group having 1 to 4 carbon atoms or taken together R¹ and R², R² and R³ or R³ and R⁴ represent the atoms necessary to complete a fused benzo ring; R⁵ represents a lower alkyl group having 1 to 4 carbon atoms; R⁶ represents hydrogen or a



group wherein R⁸ represents a heterocyclic group; and R⁷ represents a heterocyclic group. It also describes and claims a vesicular material comprising a support coated with a layer of a heat-deformable, gas-impermeable polymeric binder containing the above composition together with a method of forming a vesicular image which method comprises imagewise exposing the vesicular material to actinic radiation and heating the material sufficiently to allow the gas liberated by the vesiculating agent to expand within the polymeric binder.

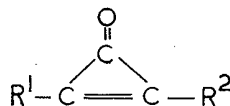
We make no claim to the invention claimed in Application No. 16448/77 (Serial No. 1584741).

Subject to the Foregoing Disclaimers

WHAT WE CLAIM IS:—

1. A vesicular imaging composition comprising: (I) a polymeric binder having sufficient gas impermeability to provide a latent image stability period as hereinbefore defined for CO that is greater than one minute when coated in a material having a dried binder thickness of from 10 to 15 microns; and (II) admixed with the binder, a radiation-decomposable vesiculating agent capable of generating CO upon imagewise exposure, the vesiculating agent being a cyclopropenone having a λ_{max} in ethanol no greater than 400 nm in the spectral range of from 250 to 650 nm.

2. A composition as claimed in Claim 1 wherein the cyclopropenone has the formula:



wherein R¹ and R² are the same or different, and are each a substituted or unsubstituted aryl radical having from 6 to 10 carbon atoms in the aromatic ring, or an aralkenyl radical having from 6 to 10 carbon atoms in the aryl portion and from 1 to 5 carbon atoms in the alkenyl portion;

the substituents of each of the substituted aryl radicals being one or more radicals selected from:

- 1) an alkyl or alkoxy radical containing from 1 to 5 carbon atoms;
- 2) a nitro radical;
- 3) an aryloxy radical containing from 6 to 10 carbon atoms;
- 4) a halogen atom; and
- 5) a polymer to which the aryl radical is attached as a dependent moiety, the

polymer having at least one repeating unit which is a lower alkylene radical containing from 1 to 5 carbon atoms.

3. A composition as claimed in Claim 2 wherein at least one of R¹ and R² is a bi-substituted aryl radical.

4. A composition as claimed in Claim 1 wherein the vesiculating agent is any one of cyclopropanone Nos. 1 to 24 hereinbefore defined.

5. A composition as claimed in Claim 1 wherein the vesiculating agent is 2 - (4 - methoxyphenyl) - 3 - phenylcyclopropanone.

6. A composition as claimed in Claim 1 wherein the vesiculating agent is 2,3 - diphenylcyclopropanone.

7. A composition as claimed in anyone of the preceding Claims further including a spectral sensitizing compound having a λ_{\max} in methanol which is less than 450 nm.

8. A composition as claimed in Claim 7, wherein the sensitizing compound is one which, when co-dissolved with a sulphonamide polymer and sufficient amounts of the cyclopropanone to photogenerate an image, forms a composition which can be dried in a layer and which upon imagewise exposure demonstrates a spectral response at a wavelength which is longer than the limit of the spectral sensitivity of the cyclopropanone.

9. A composition as claimed in Claim 7, wherein the sensitizing compound is 2 - benzoylmethylene - 3 - methyl-naphtho(2,1 - a)thiazoline.

10. A composition as claimed in Claim 7, wherein the sensitizing compound is 3 - carboxymethyl - 5 - (3 - ethylbenzothiazolinyldene)rhodanine.

11. A composition as claimed in Claim 7, wherein the sensitizing compound is anhydro - 3,3' - disulphopropyl - 5 - methoxythiacyanine hydroxide.

12. A composition as claimed in any one of the preceding Claims wherein the polymeric binder is a polymer containing toluene - 2,4 - disulphonamide units or N - (vinylphenyl) - sulphonamide units and containing at least 4 percent by weight of sulphur.

13. A composition as claimed in any one of Claims 1 to 11 wherein the polymeric binder is poly(ethylene - co - 1,4 - cyclohexylenedimethylene - 1 - methyl - 2,4 - benzenedisulphonamide).

14. A composition as claimed in Claim 1 substantially as hereinbefore described in any one of the specific Examples.

15. A vesicular imaging material comprising a support having coated thereon a composition as claimed in any one of the preceding Claims.

16. A material as claimed in Claim 15 wherein the binder is a water-insoluble, thermoplastic polymer.

17. A material as claimed in Claim 15 substantially as hereinbefore described in any one of the specific Examples.

18. A process for forming a photographic image, comprising the steps of:
a) imagewise-exposing to activating radiation a vesicular imaging material as claimed in any one of Claims 15 to 17 to form a developable latent image in the material, and

b) developing the resulting image by heating the material to a temperature and for a time sufficient to force CO bubbles formed by the photodecomposition of the vesiculating agent to expand to form a visible image.

19. A process as claimed in Claim 18 wherein the heating is carried out at a temperature within the range of from 100°C to 150°C.

20. A process as claimed in Claim 18 substantially as hereinbefore described in any one of the specific Examples.

21. A photographic image whenever formed by a process as claimed in any one of Claims 18 to 20.

L. A. TRANGMAR, B.Sc., C.P.A.,
Agent for the Applicants.

FIG. 1

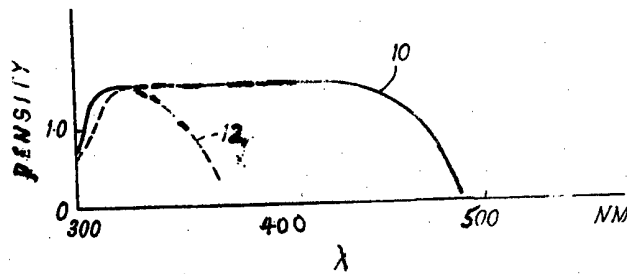


FIG. 2

