United States Patent [19]

Hughes et al.

[11] **3,885,965**

[45] **May 27, 1975**

[54] **PHOTOTHERMOGRAPHIC ELEMENT, COMPOSITION AND PROCESS**

[75] Inventors: **Donald J. Hughes; Cynthia G. Jones,** both of Rochester, N.Y.

[73] Assignee: **Eastman Kodak Company,** Rochester, N.Y.

[22] Filed: **Sept. 4, 1973**

[21] Appl. No.: **394,003**

[52] **U.S. Cl.** ..... **96/48 HD;** 96/114.1; 96/114.5; 96/114.6; 260/2 S

[51] **Int. Cl.** **G03c 1/02**

[58] **Field of Search** ..... 96/114.1, 114.5, 48 HD, 96/114.6; 260/2 S

[56] **References Cited**

UNITED STATES PATENTS

2,652,428	9/1953	Weissberger et al.	96/66 R X
2,749,253	6/1956	Shoemaker	117/36.8
3,042,522	7/1962	Ezra	96/87 R
3,489,567	1/1970	McGraw	96/85
3,672,904	6/1972	De Mauriac	96/114.1

Primary Examiner—Norman G. Torchin
Assistant Examiner—Alfonso T. Suro Pico
Attorney, Agent, or Firm—R. E. Knapp

[57] **ABSTRACT**

In a photothermographic element and composition a poly(dimethylsiloxane) provides resistance to "orange peel" effects. The photothermographic material can be processed after imagewise exposure by merely overall heating the material.

8 Claims, No Drawings

PHOTOTHERMOGRAPHIC ELEMENT, COMPOSITION AND PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to photothermographic elements and compositions which have improved resistance to orange peel effects. In one of its aspects it relates to photothermographic elements containing photosensitive silver halide and a so-called oxidation-reduction image-forming combination with a hydrophobic polymeric binder. In another of its aspects it relates to a method of processing a photothermographic element to provide the described advantages.

2. Description of the State of the Art

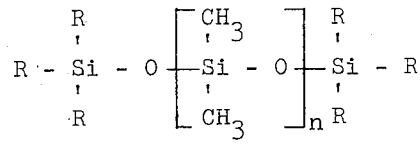
Photothermographic materials which can provide a developed image in the absence of processing solutions are well known. These materials can comprise photographic silver halide and a so-called oxidation-reduction image-forming combination comprising a silver salt oxidizing agent with a reducing agent in a polymeric binder. Typical photothermographic materials are described, for example, in U.S. Pat. No. 3,672,904 of deMauriac, issued June 27, 1972; U.S. Pat. No. 3,679,426 of Youngquist, issued July 25, 1972; U.S. Pat. No. 3,457,075 of Morgan et al., issued July 22, 1969; U.S. Pat. No. 3,152,904 of Sorensen et al., issued Oct. 13, 1964 and British Pat. No. 1,161,777 published Aug. 20, 1969. While photothermographic materials can avoid the need for processing solutions, a problem encountered in such materials is the so-called orange peel effect. This is a surface phenomenon which appears on the photothermographic element as small mounds or beads surrounded by depressed areas or boundaries and appears like the surface of an orange peel. This effect detracts from the overall quality of the image produced upon processing and is especially detrimental in microimaging. Coating aids as a class have not been found to provide resistance to orange peel in photothermographic materials. This is illustrated by the comparative examples described herein which demonstrate that such coating aids as dodecylsodium sulfate, polyethylene glycols and certain polysiloxanes do not provide suitable surface properties for the described photothermographic materials.

polysiloxanes and various silicone polymers have been employed for different purposes in photographic materials. For example, siloxane polymers have been employed as lubricants in photographic materials as described in British Pat. No. 955,061 of E. I. DuPont DeNemours published Apr. 15, 1964; U.S. Pat. No. 3,489,567 of McGraw, issued July 13, 1970; and U.S. Pat. No. 3,042,522 of Ben-Ezra, issued July 3, 1962. They have been proposed as binders as described, for example, in British Pat. No. 1,051,554 published Dec. 14, 1966 and have been employed in thermographic materials as described in U.S. Pat. No. 2,749,253 of Shoemaker et al., issued June 5, 1956.

There has been a continuing need to provide photothermographic materials which have increased resistance to orange peel effects and still provide a desired developed image upon processing with heat. There has also been a continuing need to provide addenda which can reduce the described orange peel effect without adversely affecting sensitometric properties of a photothermographic material.

SUMMARY OF THE INVENTION

It has been found according to the invention that improved resistance to orange peel effects without adversely affecting sensitometric properties is provided by the incorporation of about 0.001 to about 1.0 percent by weight of a poly(dimethylsiloxane) having units represented by the formula:



wherein R is an alkyl radical of 1 to 3 carbon atoms or an alkoxy radical of 1 to 2 carbon atoms and *n* is any number from 0 to 2000, in a photothermographic element or composition comprising (a) photosensitive silver halide and (b) a polymeric, hydrophobic binder. This photothermographic material, after exposure, can provide a developed image by merely overall heating the photothermographic material to moderately elevated temperatures, such as about 80°C. to about 250°C.

DETAILED DESCRIPTION OF THE INVENTION

Various poly(dimethylsiloxane) compounds can be employed according to the invention. The useful poly(-dimethylsiloxane) compounds must be compatible with the photosensitive components employed in that the polymers must have no deleterious sensitometric effects on the photothermographic materials and must be resistant to decomposition at processing temperatures. It is important that functional groups be avoided, such as amino substituents, which cause deleterious sensitometric properties or results. Useful poly(dimethylsiloxane) compounds can be prepared employing methods known in the polymer art. These poly(dimethylsiloxane) compounds are also commercially available and sold under such trade names as "DC-200", "DC-210", DC-710", and "DC-500" of the Dow Corning Company, U.S.A.; and such trade names as "SF-1066" and "AF-70" of the General Electric Company, U.S.A.; and "L-522"of the Union Carbide Company, U.S.A. Useful poly(dimethylsiloxane) compounds include copolymers of dimethylsiloxane with polyalkylene ethers also described as siloxaneoxymethylene or oxyethylene copolymers.

A useful embodiment of the invention is: in a photothermographic element comprising a support having thereon a photothermographic layer comprising (a) a photosensitive silver salt, (b) a polymeric, hydrophobic binder and (c) a coating aid, the improvement comprising as said coating aid about 0.001 to about 1.0 percent by weight of said layer of a poly(dimethylsiloxane) as described.

The concentration of poly(dimethylsiloxane) which is useful in a photothermographic material according to the invention, can vary depending upon the particular photothermographic material, processing conditions, components in the photothermographic material, particular poly(dimethylsiloxane) and the like. An especially useful concentration range is about 0.03 percent to about 0.6 percent by weight of the photothermo-

graphic material of the described poly(dimethylsiloxane).

A preferred embodiment of the invention is a photothermographic element comprising a support having thereon a layer comprising (a) an oxidation-reduction image-forming combination comprising (i) a silver salt oxidizing agent, such as silver behenate, with (ii) an organic reducing agent, such as a sulfonamidophenol reducing agent, (b) photosensitive silver halide, (c) a polymeric, hydrophobic binder, such as poly(vinyl butyral), (d) an activator-toning agent, and (e) about 0.001 to about 1.0 percent by weight of the layer of a poly(dimethylsiloxane) as described.

The photosensitive layers and other layers of an element according to the invention and described herein can be coated on a wide variety of supports. Typical supports include cellulose nitrate film, cellulose ester film, poly(vinyl acetal) film, polystyrene film, poly(ethylene terephthalate) film, polycarbonate film and related films or resinous materials, as well as glass, paper, metal and the like. Typically a flexible support is employed, such as a paper support which can be partially acetylated or coated with baryta and/or an alpha-olefin polymer such as a polymer of an alpha-olefin containing 2 to 10 carbon atoms such as polyethylene, polypropylene, ethylene-butene copolymers and the like.

The photothermographic elements according to the invention contain a photosensitive component. The photosensitive component is typically a photosensitive silver salt or complex, such as photosensitive silver halide and/or a complex of silver with an organic compound such as a silver dye complex. The photosensitive silver halide is especially useful as a photosensitive component because of its high photosensitivity. A typical concentration of photosensitive component in a photothermographic element according to the invention is about 0.005 to about 0.50 moles of photosensitive component per mole of oxidizing agent in the photothermographic element. Especially useful photosensitive silver halides include silver chloride, silver bromide, silver bromoiodide, silver chlorobromoiodide, or mixtures thereof. The photosensitive silver halide can be coarse or fine grain, very fine grain silver halide being especially useful. The photosensitive silver halide can be prepared by any of the procedures known in the photographic art. Such procedures and forms of photosensitive silver halide are described, for example, in the Product Licensing Index, Vol. 92, December 1971, publication 9232, pages 107–110, paragraph I.

If desired, the photosensitive silver halide employed in the described photothermographic elements can be prepared in situ such as described in U.S. Pat. No. 3,457,075 of Morgan et al. issued July 22, 1969.

The photosensitive silver halide employed according to the invention can be unwashed or washed, can be chemically sensitized, can be protected against the production of fog and/or stabilized against loss of sensitivity during keeping, as described in the Product Licensing Index, Vol. 92, December 1971, publication 9232, pages 107–110, paragraphs II, III and V.

Photographic elements according to the invention can contain development modifiers that function as speed-increasing compounds, developing agents, hardeners, antistatic layers, plasticizers and lubricants, coating aids, brighteners, matting agents, spectral sensitizing dyes, absorbing and filter dyes, also as described in the Product Licensing Index, Vol. 92, December 1971, publication 9232, pages 107–110, paragraphs Iv, VI, VII, IX, XI, XIII, XIV, and XV.

The described photothermographic elements comprise an oxidation-reduction image-forming combination which contains an oxidizing agent, typically a heavy metal salt oxidizing agent. The heavy metal salt oxidizing agent can be a heavy metal salt of an organic acid such as a fatty acid which is resistant to darkening upon illumination. An especially useful class of heavy metal salts of organic acids is represented by the water insoluble silver salts of long-chain fatty acids which are stable to light. Compounds which are suitable silver salt oxidizing agents include silver behenate, silver stearate, silver oleate, silver laurate, silver hydroxystearate, silver caprate, silver myristate and silver palmitate. Silver salts can be employed as the silver salt oxidizing agents which are not silver salts of long-chain fatty acids. Such silver salt oxidizing agents which are useful according to the invention include, for example, silver benzoate, silver benzotriazole, silver terephthalate, silver phthalate, and the like. Oxidizing agents which are not silver salts can be employed if desired such as gold stearate, mercury behenate, gold behenate, and the like, but silver salts are preferred. Combinations of heavy metal salt oxidizing agents can be useful.

Reducing agents which can be employed in the described oxidation-reduction image-forming combination include, for example, substituted phenols and naphthols, for example, bis-β-naphthols. Suitable bis-β-naphthols include, for example, 2,2′-dihydroxy-1,1′-binaphthyl, 6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl, 6,6′-dinitro-2,2′-dihydroxy-1,1′-binaphthyl and/or bis-(2-hydroxy-1-naphthyl)methane. Other reducing agents which can be employed in photographic elements according to the invention include polyhydroxybenzenes such as hydroquinone silver halide developing agents, e.g., hydroquinone, alkyl-substituted hydroquinones such as tertiary butyl hydroquinone, methyl hydroquinone, 2,5-dimethyl hydroquinone and 2,6-dimethyl hydroquinone; catechols and pyrogallols; chloro-substituted hydroquinones such as chloro hydroquinone or dichloro hydroquinone; alkoxy-substituted hydroquinone such as methoxy hydroquinone or ethoxy hydroquinone; aminophenol developing agents, such as 2,4-diaminophenols and methylaminophenols; ascorbic acid developing agents such as ascorbic acid, ascorbic acid ketals and ascorbic acid derivatives; hydroxylamine developing agents; 3-pyrazolidone developing agents such as 1-phenyl-3-pyrazolidone and 4-methyl-4-hydroxymethyl-1-phenyl-3-pyrazolidone and the like. Useful reducing agents also include sulfonamidophenol reducing agents as described in U.S. application Ser. No. 272,832 of Evans and McLaen, filed July 18, 1972 now U.S. Pat. No. 3,801,321. Combinations of these reducing agents can be employed if desired.

It is often desirable to employ a so-called activator-toning agent in the photothermographic elements according to the invention to obtain a desired image. The activator-toning agent is typically useful in a range of concentration, such as a concentration of about 0.10 moles to about 1.1 moles of activator-toning agent per mole of oxidizing agent in the photothermographic element. A typical suitable activator-toning agent is a heterocyclic activator-toning agent containing at least one nitrogen atom as described in Belgian Pat. No. 766,590

issued June 15, 1971. Typical activator-toning agents include, for example, phthalimide, N-hydroxyphthalimide, N-hydroxynaphthalimide, N-potassium phthalimide, N-silver phthalimide, N-mercury phthalimide, succinimide, and/or N-hydroxysuccinimide. Other activator-toning agents which can be employed include phthalazinone, 2-acetylphthalazinone, and the like.

It is desirable in some cases to employ an image stabilizer and/or image stabilizer precursor in the described elements of the invention. Typical image stabilizers or stabilizer precursors are described, for example, in Belgian Pat. No. 768,071 issued July 30, 1971. Typical stabilizer precursors include, for example, azothioethers and blocked azole thione stabilizer precursors as described in this Belgian patent. Other stabilizers or stabilizer precursors which can be employed include those described in U.S. Pat. No. 3,707,377 issued Dec. 26, 1972.

A photothermographic element as described according to the invention can contain various colloids alone or in combination as hydrophobic polymeric vehicles and binding agents in various layers. Suitable materials which are useful as binding agents are typically hydrophobic although some hydrophilic materials can be employed in combination with the hydrophobic materials if desired. They are transparent or translucent and include those described in U.S. Pat. No. 3,672,904 of deMauriac, issued June 27, 1972. Especially useful high molecular weight materials and resins include poly(vinyl butyral) cellulose acetate butyrate, polymethylmethacrylate, poly(vinyl pyrrolidone), ethylcellulose, polystyrene, poly(vinyl chloride), chlorinated rubber, polyisobutylene, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, copolymers of vinyl acetate, vinyl chloride and maleic acid and polyvinyl alcohol.

The photosensitive layers and other layers according to the invention can be coated by various coating procedures including dip coating, air knife coating, curtain coating or extrusion coating using hoppers such as described in U.S. Pat. No. 2,681,294 of Beguin issued June 15, 1954. If desired, two or more layers can be coated simultaneously such as described in U.S. Pat. No. 2,761,791 of Russell issued Sept. 4, 1956 and British Pat. No. 837,095.

Spectral sensitizing dyes can be used in the described photothermographic materials of the invention to confer additional sensitivity to the materials of the invention. Useful sensitizing dyes are described, for example, in the Product Licensing Index, Vol. 92, Dec. 1971, publication 9232, pages 107–110, paragraph XV.

After exposure of the described photothermographic element according to the invention, the resulting latent image can be developed merely by heating the element to moderately elevated temperatures. This merely involves heating the described photothermographic element overall to about 80°C. to about 250°C. such as for about 0.5 seconds to about 60 seconds. By increasing or decreasing the length of time of heating, a higher or lower temperature within the described range can be employed depending upon the desired image. A developed image is typically produced within several seconds, such as about 0.5 seconds to about 60 seconds.

Any suitable means can be used for providing the desired processing temperature range. The heating means can be a simple hot plate, iron, roller or the like.

Typically, a photothermographic element, as described, contains a protective layer on the photosensitive layer of an element as described. This enables contacting of the heating means with the side of the photothermographic element containing the protective layer. Accordingly, the described photothermographic element can comprise multiple layers. If desired, one or more components of the photothermographic element can be in one or more layers of the element. For example, in some cases, it can be desirable to include certain percentages of the described poly(dimethylsiloxane), reducing agent, activator-toning agent, image stabilizer or stabilizer precursor in the protective layer. In some cases this can reduce migration of certain addenda throughout the layers of the photothermographic element.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

This is a comparative example.

An acetone-toluene solution (1:1 by volume) containing 7% by weight poly(vinyl butyral) is coated on a poly(ethylene terephthalate) film support at 7.5 grams of the solution per square foot of support. The solution also contains a black dye (nigrosine dye) which facilitates observation of visual detection of the orange peel effect on the coating. Upon drying, the resulting coating is observed. A photomicrograph of a cross section of the dried coated support clearly shows the orange peel effect.

EXAMPLE 2

The procedure described in Example 1 is repeated with the exception that the described solution also contains 0.005 percent by weight of a poly(dimethylsiloxane) sold under the trade name of "Silicone AF-70" by the General Electric Company, U.S.A. Upon drying, the coating is observed to be free of orange peel effect. Similar results are obtained when an identical concentration of the described poly(dimethylsiloxane) is added to an acetone-toluene composition containing 5% by weight poly(vinyl butyral) rather than 7% by weight poly(vinyl butyral).

EXAMPLE 3

Results similar to those observed in Example 2 are obtained when the procedure is repeated as in Example 2 with the exception that a so-called dimethylsiloxane polyalkylene ether copolymer is employed in place of "Silicone AF-70". The dimethylsiloxane ether copolymer is sold under the trade name "SF-1066" by the General Electric Company, U.S.A. 0.025 percent by weight of the "SF-1066" is employed in the acetone-toluene solution.

EXAMPLE 4

A photothermographic material is prepared as follows:

A silver behenate dispersion (designated as dispersion A) is prepared by ball-milling the following components for 100 hours:

silver behenate	50.0	g
poly(vinyl butyral)	15.0	g
phthalimide	5.0	g
methylisopropyl ketone	500.0	ml

-Continued

A photosensitive composition is prepared as follows:

silver bromide composition containing poly(vinyl butyral) (100 grams of poly(vinyl butyral) per mole of silver; 6 liters emulsion/mole Ag)	160.0	ml
methanol solution containing 0.66% by weight anhydro-9-ethyl-3,3'-di(3-sulfopropyl)-4,5;4',5'-dibenzothiocarbocyanine hydroxide sodium salt	48.0	ml
silver behenate dispersion A (as described)	400.0	ml
acetone solution containing 14% by weight poly(vinyl butyral)	144.0	ml
acetone solution containing 6.3% by weight 2,2'-dihydroxy-1,1'-binaphthyl	144.0	ml
acetone solution containing 5% by weight 2,4-dihydroxybenzophenone	40.0	ml
acetone-toluene solution (1:1 by volume) containing 2% by volume poly(dimethylsiloxane) "AF-70" sold by General Electric Company, U.S.A.)	24.0	ml

The described photosensitive composition is mixed well and then coated on a poly(ethylene terephthalate) film support at 10 milliliters per 929 square centimeters. This provides a photothermographic element comprising about 100 milligrams of silver per 929 square centimeters of support. The dried coating is exposed imagewise to tungsten light and then overall heated at 135°C. for 3 seconds. No orange peel effect is observed on the photothermographic element. Also, no adverse sensitometric effects are observed on the photothermographic element.

EXAMPLE 5

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that a polyethylene glycol comprising 0.025% by weight of the solution is employed in the described coating. The polyethylene glycol has an average molecular weight of about 20,000. The resulting coating exhibits orange peel effect.

EXAMPLE 6

This is a comparative example.

The procedure set out in Example 1 is repeated with the exception that 0.025% by weight of dodecyl sodium sulfate is employed in the described acetone-toluene solution. The coating produced is observed to have orange peel effect.

EXAMPLE 7

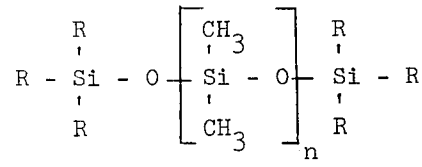
This is a comparative example.

The procedure set out in Example 4 is repeated with the exception that the siloxane polymer "DC-530" sold by the Dow Corning Corporation is employed in place of the siloxane polymer designated as "AF-70" sold by the General Electric Company, U.S.A. The siloxane polymer designated as "DC-530" is a poly(dimethylsiloxane) which contains amino substituents on the methyl groups. The resulting photothermographic material upon processing is observed to have orange peel and undesired printout density formation is observed.

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

What is claimed is:

1. In a photothermographic element comprising a support having thereon a photothermographic layer comprising (a) a photosensitive silver salt, (b) a polymeric, hydrophobic binder and (c) a coating aid, the improvement comprising as said coating aid about 0.001 to about 1.0 percent by weight of said layer of a poly(dimethylsiloxane) having units represented by the formula:

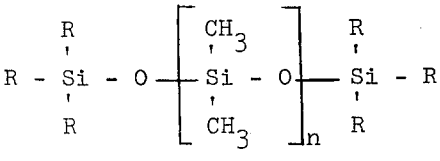


wherein R is an alkyl radical of 1 to 3 carbon atoms or an alkoxy radical of 1 to 2 carbon atoms and *n* is any number from 0 to 2000.

2. A photothermographic element as in claim **1** wherein said coating aid is a siloxane oxymethylene copolymer.

3. A photothermographic element comprising a support having thereon a layer comprising

a. an oxidation-reduction image-forming combination comprising
   i. a silver salt oxidizing agent with
   ii. an organic reducing agent,
b. photosensitive silver halide,
c. a polymeric, hydrophobic binder,
d. an activator-toning agent, and
e. about 0.001 to about 1.0 percent by weight of said layer of a poly(dimethylsiloxane) having units represented by the formula:



wherein R is an alkyl radical of 1 to 3 carbon atoms or an alkoxy radical of 1 to 2 carbon atoms and *n* is any number from 0 to 2000.

4. A photothermographic element as in claim **3** comprising a support having thereon a layer comprising

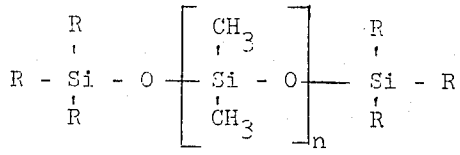
a. an oxidation-reduction image-forming combination comprising
   i. silver behenate with
   ii. a sulfonamidophenol reducing agent,
b. photosensitive silver salt,
c. poly(vinyl butyral) binder,
d. an N-hydroxynaphthalimide or succinimide activator-toning agent, and
e. about 0.001 to about 1.0 percent by weight of said layer of poly(dimethylsiloxane).

5. A photothermographic composition comprising

a. photosensitive silver salt,
b. a polymeric, hydrophobic binder,
c. an oxidation-reduction image-forming combination comprising
   i. a silver salt oxidizing agent, with

ii. a reducing agent and

d. about 0.001 to about 1.0 percent by weight of said composition of a poly(dimethylsiloxane) having units represented by the formula:



wherein R is an alkyl radical of 1 to 3 carbon atoms or an alkoxy radical of 1 to 2 carbon atoms and *n* is any number from 0 to 2000.

6. A photothermographic composition as in claim **5** comprising

a. photosensitive silver salt,

b. a poly(vinyl butyral) binder,

c. an oxidation-reduction image-forming combination comprising

i. silver behenate with

ii. a sulfonamidophenol reducing agent,

d. an N-hydroxynaphthalimide or succinimide activator-toning agent, and

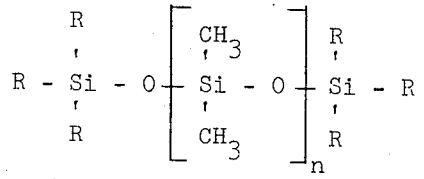
e. about 0.001 to about 1.0 percent by weight of said composition of poly(dimethylsiloxane).

7. A method of developing a latent image in a photothermographic element comprising a support having thereon a photothermographic layer comprising

a. photosensitive silver salt,

b. a polymeric, hydrophobic binder and

c. about 0.001 to about 1.0 percent by weight of said layer of a poly(dimethylsiloxane) having units represented by the formula:



wherein R is an alkyl radical of 1 to 3 carbon atoms or an alkoxy radical of 1 to 2 carbon atoms and *n* is any number from 0 to 2000, comprising heating said element within the range of about 80°C. to about 250°C. until said image is developed.

8. A method as in claim **7** of developing a latent image in a photothermographic element comprising a support having thereon a layer comprising

a. an oxidation-reduction image-forming combination comprising

i. silver behenate with

ii. a sulfonamidophenol reducing agent,

b. photosensitive silver salt,

c. poly(vinyl butyral) binder,

d. an N-hydroxynaphthalimide or succinimide activator-toning agent, and

e. about 0.001 to about 1.0 percent by weight of said layer of poly(dimethylsiloxane),

comprising heating said element within the range of about 80°C. to about 250°C. until said image is developed.

* * * * *