June 2, 1970 TAKASHI SUZUKI 3,515,570

HEAT-SENSITIVE SHEET AND METHOD OF THERMOGRAPHIC REPRODUCTION USING THE SAME

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FIG. 1

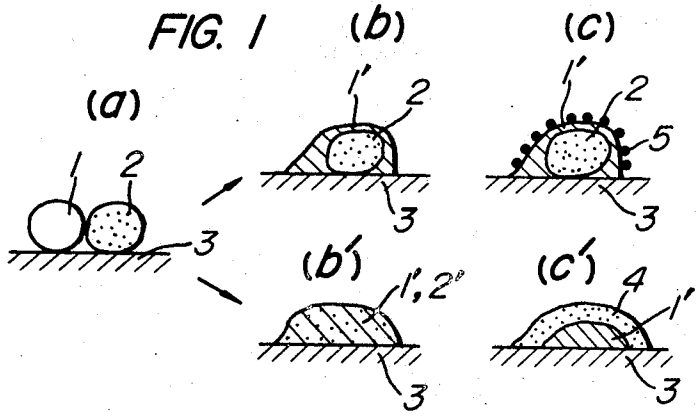
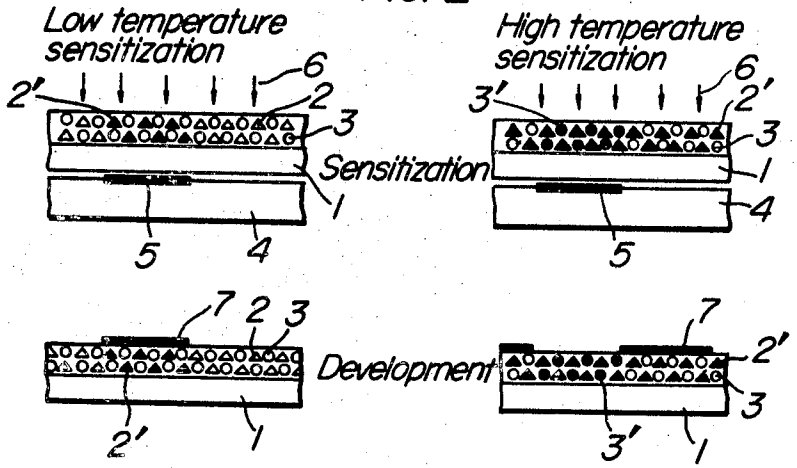


FIG. 2



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HEAT-SENSITIVE SHEET AND METHOD OF THERMOGRAPHIC REPRODUCTION USING THE SAME

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U.S. Cl. 117—25 2 Claims

ABSTRACT OF THE DISCLOSURE

A heat-sensitive sheet comprising a support, and a heat-sensitive layer coated on said support, said heat-sensitive layer containing fine solid particles of a first material which shows a stable supercooling property and has a melting point of 45° C. to 120° C. and fine solid particles of a second material which does not show any stable supercooling property and has a melting point at least 10° C. higher than the melting point of said first material, said heat-sensitive layer being such that both said fine particles appear on the surface when they are heated to melt and the surface of said heat-sensitive layer is covered with said second material not showing any stable supercooling property when the fine particles of both said materials are cooled after being melted and a method of thermographic reproduction using said heat-sensitive sheet.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part application of U.S. patent application Ser. No. 514,792, Dec. 20, 1965, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a method of thermographic reproduction utilizing the supercooling property of a certain material and development by a powder developer and also to a heat-sensitive sheet for use in such a method.

Description of the prior art

It is known in the art that a certain material has such a property that it does not solidify and remains in its liquid state even when heated to melt and then allowed to cool down to a temperature below its melting point. This property of such a material is called the supercooling property. A thermographic reproduction system can be provided by a suitable combination of this supercooling property inherent to a specific material and a wetting phenomenon of solid particles in the liquid state. More precisely, when fine solid particles of a material showing a stable supercooling property when heated to melt are uniformly dispersed on the surface of a support to provide a heat-sensitive sheet and heat exposure is performed in accordance with common heat exposure practice on the heat-sensitive sheet, a positive latent image consisting of fine supercooled liquid particles is formed on the heat-sensitive sheet. By applying to the positive latent image a powder developer (toner) such as is commonly employed in the art of electrophotography, the fine supercooled liquid particles wet the surface of the toner and fix the toner on the heat-sensitive sheet, thereby giving a positive visible image.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a heat-sensitive sheet of unique structure.

Another object of the present invention is to provide a method of thermographic reproduction for obtaining a negative image by use of such a heat-sensitive sheet.

In accordance with the present invention, there is provided a heat-sensitive sheet comprising a support, and a heat-sensitive layer coated on said support and containing fine solid particles of a first material which shows a stable supercooling property and has a melting point of 45°C. to 120° C. and fine solid particles of a second material which does not show any stable supercooling property and has a melting point at least 10° C. higher than the melting point of said first material, said heat-sensitive layer being such that the fine particles of both said materials appear on the surface when they are heated to melt, and the surface of said heat-sensitive layer is covered with said second material not showing any stable supercooling property when the fine particles of both said materials are cooled down after being melted.

In accordance with the present invention, there is also provided a method of thermographic reproduction comprising the steps of superposing said heat-sensitive sheet on an original, exposing the exposure sandwich to heat in such a manner that the temperature of said heat-sensitive sheet at those portions corresponding to an image carried by the original becomes higher than the melting point of said second material not showing any stable supercooling property while the temperature of said heat-sensitive sheet at those portions corresponding to the background lies between the melting point of said first material showing the stable supercooling property and the melting point of said second material not showing any stable supercooling property, and developing said heat-sensitive sheet by a powder developer to obtain a negative image.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an explanatory view showing the process of changes taking place in the heat-sensitive sheet according to the present invention; and

FIG. 2 is a schematic view showing how a positive copy and a negative copy can be obtained with the heat-sensitive sheet according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

One of the important features of the present invention resides in the fact that supercoolable particles coexist with non-supercoolable particles within a heat-sensitive sheet. Hereinafter, the mechanism of heat sensitization in the sheet containing such supercoolable and non-supercoolable particles will be described in detail. The mechanism of heat sensitization has been clarified by microscopic examination of the surface of the heat-sensitive sheet by the inventor.

On the surface of the heat-sensitive sheet according to the present invention, fine solid particles (hereinafter to be referred to as supercoolable particles) showing a stable supercooling property when heated to melt coexist with fine solid particles (hereinafter to be referred to as non-supercoolable particles) do not showing any supercooling property when heated to melt.

In FIG. 1*a*, supercoolable particles **1** and non-supercoolable particles **2** are shown fixed in their solid state on a support **3** as they are not yet exposed to heat. Suppose now that heat is applied from a source of heat at a temperature lower than the melting point of the non-supercoolable particles **2** but higher than the melting point of the supercoolable particles **1** (this heat sensitization

being hereinafter referred to as low-temperature sensitization). Then, the supercoolable particles **1** are solely melted in a manner as shown by **1'** in FIG. 1*b* and wet the surface of the non-supercoolable particles **2**. Since the molten supercoolable particles **1'** remain in their liquid state even after removal of the source of heat, particles of a powder developer (toner) **5** adhere to the molten supercoolable particles **1'** during development with the toner as shown in FIG. 1*c*. In case heat is applied at a temperature higher than the melting point of the non-supercoolable particles **2** (this heat sensitization being hereinafter referred to as high-temperature sensitization), both the particles **1** and **2** are melted to form single particles consisting of a mixture of the molten supercoolable particles **1'** and the molten non-supercoolable particles **2'** as shown in FIG. 1*b'*. In the course of subsequent cooling, the non-supercoolable particle component solidifies quickly to turn into a shell **4** and the solidification proceeds inwardly from the external surface of the molten particle mixture. The supercoolable particle component remains still in its liquid state and is confined within the shell **4** of the non-supercoolable particles as shown in FIG. 1*c'*.

It is possible with the heat-sensitive sheet of the present invention having such a property to obtain either a positive or a negative copy. The mechanism of obtaining a positive or negative copy is diagrammatically illustrated in FIG. 2. In FIG. 2, the reference numeral **1** denotes a support of the heat-sensitive sheet; **2**, supercoolable particles; **2'**, those supercoolable particles which are heat sensitized; **3**, non-supercoolable particles; **3'** those non-supercoolable particles which are heat sensitized; **4**, an original; **5**, an image portion on the original **4**; **6**, infrared rays; and **7**, a layer of powder developer (toner). It will easily be seen that a positive image can be obtained when heat sensitization is performed under conditions in which the heat-sensitive materials corresponding to the image portion **5** on the original **4** are subjected to low-temperature sensitization, and a negative image can be obtained when heat sensitization is made under the conditions in which the heat-sensitive materials corresponding to the image portion **5** on the original **4** are subjected to high-temperature sensitization and the heat-sensitive materials corresponding to the portions other than the image portion **5** are subjected to low-temperature sensitization.

The supercoolable material and the non-supercoolable material employed in the present invention have preferably such a nature that they intermix with each other when heated to melt to thereby form a uniform liquid. It is also desirable that, at a temperature below the melting point of the non-supercoolable particles, the non-supercoolable particle component is hardly soluble to the liquid consisting of the supercoolable particle component. It is further desirable that there is a difference of at least 10° C. between the melting point of the supercoolable particles and the melting point of the non-supercoolable particles in order to facilitate the procedure of selective melting of the supercoolable particles, that is, the low-temperature sensitization. The material suitable for forming the supercoolable particles may, for example, be an organic phosphate, aromatic amine or dye intermediate including triphenyl phosphate and a mixture of acetanilide and benzotriazol. The material suitable for forming the non-supercoolable particles may, for example, be a paraffin, higher fatty acid, higher alcohol or petroleum wax.

Good results could be obtained with the following combinations:

	Percent
Triphenyl phosphate (M.P. 49° C.)	20–80
Stearic acid (M.P. 71° C.)	80–20
Triphenyl phosphate (M.P. 49° C.)	40–90
Paraffin (M.P. 60°–62° C.)	60–10
4:6 mixture of acetanilide:benzotriazol (M.P. 60° C.)	45
Behenic acid (M.P. 79° C.)	55

The melting point of the supercoolable particles must lie within a certain limited range in order that the particles are actually heat-sensitized by an infrared ray lamp. The result of tests made by the inventor proved that a range of 45° C. to 120° C. is most suitable. The melting point of the non-supercoolable particles may be as high as 150° C. at the maximum in practical use.

It is required that these supercoolable and non-supercoolable particles are kept in a uniformly dispersed state within the heat-sensitive layer of the heat-sensitive sheet and yet they appear on the surface of the heat-sensitive layer when they are heat-sensitized. Such a heat-sensitive layer may be deposited on a support by a method comprising dispersing the supercoolable particles and non-supercoolable particles individually or in a previously mixed and melted state into an aqueous solution of a binder such as gelatine or polyvinyl alcohol and coating the dispersion on a support, or by a method comprising diluting the supercoolable material and the non-supercoolable material with a solvent which dissolves at least one of these materials, dispersing the non-dissolved material in the form of fine particles and impregnating or coating a porous support such as paper with the dispersion.

When the purpose is to obtain a negative image with a high resolution on the heat-sensitive sheet obtained in this manner, the infrared ray lamp which is the source of heat must be considerably strong and emit infrared radiation having a uniform intensity. However, such letters as are printed on a common magazine can easily be copied by use of a conventional heat-sensitive copying apparatus in combination with the heat-sensitive sheet.

Several examples of the heat-sensitive sheet according to the present invention will be described hereunder so that the present invention can more clearly be understood.

EXAMPLE 1

50 grams of triphenyl phosphate was added to 50 cc. of a 10% aqueous solution of gelatine heated to 70° C. The above composition was then emulsified in an emulsifier and allowed to cool for about five hours at room temperature. 50 grams of behenic acid was separately added to 150 cc. of another 10% aqueous solution of gelatine heated to 85° C. The above mixture was also emulsified in an emulsifier and allowed to cool down to room temperature. Then, the two solutions were mixed together and thoroughly agitated at room temperature. The mixture thus obtained was coated on a cellulose triacetate film and dried to obtain a heat-sensitive sheet. The heat-sensitive sheet was superposed on an original printed in black and the exposure sandwich was exposed to infrared rays coming from an apparatus which was made by reconstructing a conventional heat-sensitive copying apparatus (Thermofax) so as to increase the infrared ray intensity to about 1.4 times the previous value. Development was then made by the magnetic brush method using a powder developer commonly employed in electrophotography. As a result of this manner of development, a positive image could be obtained with an irradiation time of 0.5 second while a negative image could be obtained with an irradiation time of 1.0 second.

EXAMPLE 2

A mixture of 50 grams of triphenyl phosphate and 50 grams of stearic acid was heated to melt, and 300 cc. of a 10% aqueous solution of gelatine heated to 85° C. was added to the mixture. The above composition was then emulsified in an emulsifier, and the emulsion thus obtained was ooated on a cellulose triacetate film to obtain a heat-sensitive sheet. This heat-sensitive sheet was exposed to heat in the same manner as in Example 1. As a result, a positive image could be obtained with an irradiation time of 0.5 second while a negative image could be obtained with an irradiation time of 0.8 second. The resolutions of the positive image and the negative image

were 4 lines per millimeter and 3 lines per millimeter, respectively.

EXAMPLE 3

5 grams of triphenyl phosphate and 3 grams of paraffin (melting point 60° to 62° C.) were dissolved in a mixed solution of 50 cc. of ethyl alcohol and 50 cc. of toluene. A sheet of tracing paper was impregnated with the above composition and was left to stand at room temperature for a while until the solvent was evaporated. The heat-sensitive sheet thus obtained was exposed to heat in the same manner as in Example 1. As a result, a positive image could be obtained with an irradiation time of 0.7 second while a negative image could be obtained with an irradiation time of 1.1 seconds.

The matter to which attention should be directed in this respect is the fact that, in Examples 2 and 3, the supercoolable material and the non-supercoolable material are mixed and melted or are made into the form of fine particles after mixing and melting. While it is yet unknown as to in what state the supercoolable material and the non-supercoolable material are distributed within the heat-sensitive layer finally obtained in these cases, it is supposed that the state of FIG. 1*c'* in which the supercoolable material is confined within the non-supercoolable material does not occur within the heat-sensitive layer. This is because the supercoolable material appears on the surface of the heat-sensitive layer as a result of low-temperature sensitization, and this portion becomes adhesive to the toner. Further, the reason is not clear why the triphenyl phosphate in the heat-sensitive layer remains in the solid state and does not remain in its supercooled state after the heat-sensitive sheet according to Example 2 has been manufactured. The same applies to Example 3. It seems that, during the formation of the heat-sensitive layer in these examples, water or solvent vaporizes from the heat-sensitive layer thereby destroying the state of supercooling and giving rise to crystal formation of a form which is different from the case in which a melt is merely cooled.

It will be appreciated from the foregoing description that a positive or a negative image can be obtained on the same sheet at will by employing the heat-sensitive sheet and the method of thermographic reproduction according to the present invention. The heat-sensitive sheet and the method of thermographic reproduction are industrially quite valuable as they can be made and performed with a very simple process.

What is claimed is:

1. A heat-sensitive sheet comprising a support, and a heat-sensitive layer coated on said support, said heat-sensitive layer containing fine solid particles of a first material which shows a stable supercooling property and has a melting point of 45° C. to 120° C. and fine solid particles of a second material which does not show any stable supercooling property and has a melting point at least 10° C. higher than the melting point of said first material, the supercoolable particles being meltable at low heat to wet the surface of the non-supercoolable particles while at above the fusion temperature of both types of particles they both melt to merge together in molten state and upon subsequent cooling, the non-supercoolable particles solidify to form a shell about the supercoolable liquid particles.

2. A method of thermographic reproduction comprising the steps of superposing a heat-sensitive sheet as claimed in claim **1** on an original, exposing the exposure sandwich to heat in such a manner that the temperature of said heat-sensitive sheet at those portions corresponding to an image carried by the original becomes higher than the melting point of said second material not showing any stable supercooling property while the temperature of said heat-sensitive sheet at those portions corresponding to the background lies between the melting point of said first material showing the stable supercooling property and the melting point of said second material not showing any stable supercooling property, and developing said heat-sensitive sheet by a powder developer to obtain a negative image.

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