

1

3,674,538

HEAT-SENSITIVE SHEET

Takashi Suzuki, Ikeda-shi, Japan, assignor to Matsushita Electric Industrial Co. Ltd., Osaka, Japan

No Drawing. Continuation-in-part of application Ser. No. 514,800, Dec. 20, 1965. This application Apr. 8, 1969, Ser. No. 814,433

Int. Cl. B41m 5/26

U.S. Cl. 117—36.7

6 Claims

ABSTRACT OF THE DISCLOSURE

A heat-sensitive sheet using a mixture of p-cresyl phosphate and other organic phosphoric acid esters such as triphenyl phosphate, tributyl phosphate, 2-ethylhexyl phosphate and mixtures of tricresyl phosphate isomers.

CROSS-REFERENCES TO RELATED APPLICATION

This is a continuation-in-part of application Ser. No. 514,800 filed on Dec. 20, 1965, and now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to a heat-sensitive sheet for reproduction using the supercooling property.

The method of thermographic reproduction using supercoolable liquid and powder developer has been publicly known. According to this method, the heat-sensitive material of a copying sheet is made of a substance which is solid at room temperature but has good supercooling property when melted and liquefied. The copying sheet is superposed on an original, and intense infrared ray is irradiated thereon to raise the temperature on the image portion of the original and melt the heat-sensitive material. This melting state still remains after the removal of the heat source. The powder developer introduced to this state adheres to the surface of the melting liquid whereby an image is obtained.

This invention is related to such a heat-sensitive copying sheet as is used in the above-method.

Description of the prior art

Inorganic substances having good supercooling property heretofore obtained are sulphur, antimony, sodium hyposulfite, and sodium acetate, while organic ones are acetanilide, phenacetin, benzotriazole, acetylthiocarbacid, dimedonebenzoic acid, sebacic acid, citric acid, cinnamic acid and their suitable mixtures.

The important factors are that these materials for reproduction are chemically stable, stably supercooled, colorless and odorless, harmless to the human body, have a melting point within a suitable temperature range, are free from decomposition even if heated considerably higher than the melting point, selectively dissolved in solvent, easily pulverized, and easily manufactured.

According to the inventor's experiments, the above publicly known supercoolable substances do not fully satisfy these necessary conditions. So, they are not always suitable as heat-sensitive material for reproduction.

For example, hyposulfite and sodium acetate lose a part of crystallization water at a temperature slightly higher than the melting point and change into other substances which have no more supercooling property. The manufacture of heat-sensitive sheet is easily done by diluting the heat-sensitive substance in solvent and impregnating it in a porous base. But the mixture of benzotriazole with acetanilide or with phenacetin is not suited to such a dissolution method in spite of their good supercooling

2

property. The reason is not yet clear but lies perhaps in the fact that two substances are separated from each other when the solvent is evaporated.

The inventor has found that triphenyl phosphate is a very excellent heat-service material for reproduction. Although triphenyl phosphate satisfies almost all of the above-mentioned necessary conditions, a weak point thereof is that the melting point is low, i.e. 49° C. So, when a large pressure is applied to the sheets stacked for preservation, they are softened so that the possibility arises that they will adhere to each other. Another weak point is that the heat-sensitive temperature differs only a little from the room temperature. Unless the infrared source is very strong and uniform, it is difficult to copy distinguishably the thin and thick lines drawn in the original.

SUMMARY OF THE INVENTION

Therefore, the purpose of this invention is to improve such shortcomings as mentioned above and to provide a heat-sensitive material for reproduction with a melting point between 65° and 100° C. satisfying the aforementioned conditions.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The inventor has found that the mixture of p-tricresyl phosphate with other phosphoric esters is very suitable for the above-mentioned objects.

p-tricresyl phosphate is a colorless, incombustible and stable substance having a melting point in the range from 77 to 78° C. But its supercooling property is not satisfactory for the copying heat-sensitive material. However, if other phosphoric esters are added, the supercoolness is found to be remarkably improved, yielding a very suitable heat-sensitive material. The esters are triphenyl phosphate, tricresyl phosphate mixed with isomers that are customarily used as plasticizer, tributyl phosphate, and 2-ethylhexylphosphate and the like. When the amount of such additives is increased the supercooling property is promoted but the melting point is decreased. This tendency is similar with all adding agents but the degree differs with the kind of esters.

With a 40% addition of triphenyl phosphate the melting point becomes 69° C. while with a 40% addition of tricresyl phosphate mixed with isomers it becomes about 60° C. Tricresyl mixed isomers are, of course, a mixture of o-tricresyl phosphate, m-tricresyl phosphate and p-tricresyl phosphate.

When the formation of the sheet is performed by diluting the heat-sensitive substance in solvent and impregnating it in a porous base, a 10% addition of the above-mentioned esters yields the best supercooling property. When the heat-sensitive material is obtained by being dispersed in aqueous solutions of polyvinyl alcohol, gelatine and the like and thereafter coated on a base, a 1 to 20% addition of them yields good results. Similar results are obtained with other kinds of phosphoric ester.

From the above results the most preferable composition of the heat-sensitive material is 99 to 65% of p-tricresyl phosphate and 1 to 35% of other phosphoric esters.

However, the above-mentioned composition does not always remain the best for other manufacturing methods and fabrication conditions. The composition is not restrictive.

Next, the embodiments will be described.

EXAMPLE 1

p-Tricresyl phosphate 1.6 g. triphenyl phosphate 0.4 g. were dissolved in toluene 1000 cc. A sheet of frosted tracing paper was dipped in the above solution, pulled out and dried at room temperature. The sheet was superposed on an original, which was a sheet of high quality

3

paper printed with black ink. A 375 w. infrared lamp was irradiated for about 3 seconds from 2 cm. above the sheet. The heat-sensitive sheet was developed by powder developer used in electrophotography. As a result, a good copy was obtained.

EXAMPLE 2

p-Tricresyl phosphate 8.8 g. and tricresyl phosphate mixed isomers 1 g. were heated at 90° C. to 110° C. for 10 minutes and flowed into 5% aqueous solution of polyvinyl alcohol 100 cc. They were mixed and dispersed by a juice mixer, and coated 10 to 50 μ thick on a triacetyl cellulose film of 0.05 mm. thickness. The heat-sensitive sheet was examined under the same condition as in embodiment 1. About 2 minutes irradiation of an infrared lamp yielded a copy.

As is evident from the foregoing description, this invention relates to a heat-sensitive sheet using a heat-sensitive substance made of a mixture of p-tricresyl phosphate and other kinds of phosphoric ester. By a suitable selection of their composition ratio the heat-sensitive sheet can have the best thermographic temperature, supercooling property and stability.

I claim:

1. A sheet for thermographic reproduction having a heat sensitive coating thereon which is normally crystalline at room temperature but super cools and remains liquid after it has been melted comprising as the material which super cools a mixture of p-tricresyl phosphate and other organic phosphoric acid esters selected from the group consisting of triphenyl phosphate, tributyl phosphate, 2-ethylhexyl phosphate and a mixture of tricresyl phosphate isomers.

2. A sheet according to claim 1 wherein said organic phosphoric acid esters are selected from the group consisting of triphenyl phosphate and a mixture of tricresyl phosphate isomers.

4

3. The sheet of claim 1 wherein the p-tricresyl phosphate is mixed with triphenylphosphate.

4. The sheet of claim 1 wherein said mixture contains a mixture of tricresyl phosphate isomers.

5. The sheet of claim 1 wherein the mixture contains from about 65% to about 99% p-tricresyl phosphate and from about 1% to about 35% of said other organic phosphoric acid esters.

6. The sheet of claim 1 wherein the heat sensitive coating has a melting point between 65° and 100° C.

References Cited

UNITED STATES PATENTS

15	1,997,583	4/1935	Hitt	117—122 X
	2,629,671	2/1953	Murray	117—8
	3,121,650	2/1964	Meissner	156—240
	3,256,811	6/1966	Bach	117—1.7 X
	3,360,367	12/1967	Stricklin	117—1.7 X
20	3,260,612	7/1966	Dulmage et al.	117—25
	3,261,023	7/1966	Light et al.	117—37
	3,362,380	1/1968	Anderson et al.	250—65.1 X
	3,364,858	1/1968	Kojima et al.	101—467
	3,079,253	2/1963	Greig	117—17.5 X
25	3,493,412	2/1970	Johnston et al.	96—1.4 X

OTHER REFERENCES

Noller, 1957, page 515.

30 WILLIAM D. MARTIN, Primary Examiner
B. D. PIANALTO, Assistant Examiner

U.S. Cl. X.R.

35 117—17.5, 25, 122 H, 154, 161 UE