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EP 0 210 852 A2 (54) Films for use as stencils in mimeograph printing.

(57) A film for use as a stencil in mimeograph printing and which is prepared from a composition comprising 70 to 90% by weight of polypropylene resin, 30 to 10% by weight of electroconductive carbon black and 0.05 to 3 parts by weight, per 100 parts by weight of the total amount of the polypropylene resin and electroconductive carbon black of organofunctional silane, titanate and/or aluminate.

FILMS FOR USE AS STENCILS IN MIMEOGRAPH PRINTING

This invention relates to films for use as stencils in mimeograph printing and which comprise polypropylene resin and electro-conductive carbon black. The films exhibit excellent ink solvent resistance in mimeograph printing and uniform perforatability on being subjected to electrical discharge treatment.

A film prepared by uniformly kneading a polyvinyl chloride resin, an electroconductive carbon black and additives such as a plasticizer and a stabilizer, and molding the resultant mixture, has conventionally been used as a stencil employed in mimeograph printing. The film is used as a stencil by superposing the film on a base paper constituted by high quality paper bearing an electroconductive layer comprising electroconductive carbon black and a binder, perforating the film by electrical discharge treatment and then peeling it off the base paper. However, such a film comprising polyvinyl chloride resin gives off hydrogen chloride gas because of the heat generated when the film is perforated by the electrical discharge treatment, and therefore poses problems of hygiene and also of corrosion of the electrical discharge device being employed.

Use of a polyolefin resin such as polyethylene resin or polypropylene resin is regarded as overcoming the above problem. The film formed of such a resin does not generate gas having unpleasant odor, but on the other hand the use of polyethylene resin for forming the film used as a stencil raises the problem that the film is swollen by oils or solvents contained in printing ink; the film consequently becomes elongated during mimeograph printing, resulting in formation of wrinkles, and sharp prints cannot be obtained.

Conversely, the use of polypropylene resin does not entail any great problem over ink solvent resistance during printing, but it does raise the problem that a composition to which a large amount of electroconductive carbon black has been added is difficult to mold into a film having a uniform thickness; as a result the perforating properties required for use as a stencil become non-uniform and, therefore, the amount of carbon black that can be added is limited.

Accordingly, one aim of the present invention is to overcome the problems arising from non-uniform perforatability during electrical discharge treatment normally encountered when using a composition comprising a polypropylene resin and an electroconductive carbon black to form a film for use as a stencil in mimeograph printing.

Another aim of the present invention is to provide a film for use as a stencil in mimeograph printing and which does not generate gas having unpleasant odor when the film is perforated by electrical discharge treatment; which has excellent ink solvent resistance during mimeograph printing; and which has uniform perforating properties during electrical discharge treatment even when a large amount of carbon black is incorporated in the film.

The film according to the present invention for use as a stencil in mimeograph printing is prepared from a composition comprising from 70 to 90% by weight of a polypropylene resin, from 30 to 10% by weight of an electroconductive carbon black, and from 0.05 to 3 parts by weight, per 100 parts by weight of the total amount of the polypropylene resin and electroconductive carbon black, of an organofunctional compound selected from organofunctional silanes, organofunctional titanates and organofunctional aluminates.

Examples of the polypropylene resin which can be used in the present invention include propylene homopolymers, and copolymers of propylene and ethylene, butene-1, hexene-1, 4-methylpentene-1, octene-1 or the like. Of these, a crystalline propylene homopolymer is preferred. The crystalline propylene homopolymer has a density of at least 0.903 g/cm³, preferably at least 0.904 g/cm³, and a crystallinity of at least 62% (calculated from the density), preferably 63 to 70%. If the density is less than 0.903 g/cm³, the ink solvent resistance is poor; and elongation of the film occurs during mimeograph printing, resulting in the formation of wrinkles, and unclear prints tend to be obtained. These defects may also occur in the case of using a copolymer of propylene with ethylene or the like.

Examples of the electroconductive carbon black which can be used in the present invention include acetylene black, furnace black, thermal black, specific furnace black (Ketjen Black, a registered trademark), and the like. These carbon blacks can be used alone or as mixtures thereof.

The amount of the polypropylene resin used is from 70 to 90% by weight, preferably from 75 to 85% by weight, and the amount of the electroconductive carbon black used is from 30 to 10% by weight, preferably from 25 to 15% by weight, based on the total weight of the polypropylene resin and the electroconductive carbon black. If the amount of the electroconductive carbon black is less than 10% by weight, sufficient perforation cannot be obtained with electrical discharge treatment.

On the other hand, if the amount thereof is more than 30% by weight, film formation is difficult, the film obtained is brittle or the film breaks during electrical discharge treatment.

Furthermore, mineral oils such as paraffinic, naphthenic or aromatic processing oils which are conventionally used as softening agents for rubbers, fluid paraffin, and vegetable oils such as castor oil, cottonseed oil, linseed oil, rapeseed oil, soybean oil and peanut oil, can be added to the composition in an amount of from 0.1 to 25 parts by weight, preferably from 0.5 to 15 parts by weight, per 100 parts by weight of the polypropylene resin. The addition thereof can provide a film for use as a stencil in mimeograph printing which has good perforatability, even at high speed, during electrical discharge treatment, and no propensity to curl.

The organofunctional compound selected from organofunctional silanes, organofunctional titanates and organofunctional aluminates which can be used in the present invention is a compound such as is used as a coupling agent in glass-fiber reinforced thermosetting resins and thermoplastic resins. Examples of organofunctional silanes include vinyl triethoxysilane, vinyl trichlorosilane, vinyl tris(β -methoxyethoxy)silane, γ -methacryloxypropyltrimethoxysilane, γ -glycidoxypolytrimethoxysilane, β -(3,4-epoxycyclohexyl)-ethyltrimethoxysilane, γ -aminopropyltriethoxysilane, γ -aminodithiopropyltriethoxysilane, N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane, N-bis-(β -hydroxyethyl)- γ -aminopropyltriethoxysilane, γ -chloropropyltrimethoxysilane and γ -mercaptopropyltrimethoxysilane.

Examples of organofunctional titanates include isopropyltriisostearoyltitanate, isopropyltridodecylbenzenesulfonyltitanate, isopropyltris-(dioctylpyrophosphate)titanate, tetraisopropylbis-(dioctylphosphite)titanate, tetraoctylbis-(ditridycelphosphite)titanate, tetra(2,2-diallyloxymethyl-1-butyl)bis(di-tridycelphosphite)-titanate and bis(dioctylpyrophosphate)-oxyacetatetitanate, bis(dioctylpyrophosphate)ethylenetitanate. Examples of organofunctional aluminates include acetoalkoxyaluminum-diisopropylate.

The organofunctional compound is used in an amount of from 0.05 to 3 parts by weight, preferably from 0.1 to 1.5 parts by weight, per 100 parts by weight of the total amount of the polypropylene resin and the electroconductive carbon black. If the amount of the organofunctional compound is less than 0.05 parts by weight, it is difficult to form the composition into a film having a uniform thickness and its perforating properties consequently become non-uniform. On the other hand, if the amount

thereof is more than 3 parts by weight, a beneficial effect from further addition cannot be expected, and extrusion to form a film cannot be conducted in a stable manner.

The components described above are kneaded in a conventional mixing machine such as a Banbury mixer, rolls or a single- or twin-screw extruder, and the mixture obtained is subjected to film-forming processing. In order to avoid secondary agglomeration of the particles of the carbon black, a conventional additive such as zinc stearate may be used. The film is molded by a T-die casting method, a tubular method using a circular die, or a like method.

The thickness of the film according to the present invention for use as a stencil in mimeograph printing is preferably 10 to 30 μ m. If the thickness is less than 10 μ m, the film strength after perforation is poor; and if the thickness is more than 30 μ m, the perforations are not sufficiently sharp, and clear prints cannot be obtained.

The film according to the present invention for use as a stencil in mimeograph printing has the advantages that, since a polypropylene resin is used, gas having unpleasant odor is not generated when the film is perforated by an electrical discharge treatment and the ink solvent resistance is excellent, and as a result, there is no problem of film elongating during mimeograph printing, resulting in formation of wrinkles and consequent failure to obtain clear prints.

Furthermore, due to the use of an organofunctional compound, a film having a uniform thickness can be obtained, and as a result, the film exhibits uniform perforatability during electrical discharge treatment.

The present invention is illustrated in greater detail in the following Examples and Comparative Examples. Unless otherwise indicated, all percentages and parts are by weight.

EXAMPLE 1

80% of a crystalline propylene homopolymer having a density of 0.904 g/cm³ ("Mitsubishi Norbrene FY6F", a product of Mitsubishi Petrochemical Co., Ltd.), 20% of acetylene black (a product of Denki Kagaku Kogyo K.K.), and 0.5 part, per 100 parts of the total amount of the crystalline propylene homopolymer and acetylene black, of N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane ("A-1120", a product of Nippon Unicar Co., Ltd.) were melt-kneaded in a Banbury mixer at 220°C for 10 minutes at 80 rpm. The resulting composition was extruded by T-die at a resin temperature of 200°C

using an extruder having L/D of 24 and a diameter of 65 mm to obtain a film for use as a stencil in mimeograph printing and having a thickness of 20 μ m. The molding speed was 18 m/min.

The film was superposed on an electroconductive base paper, and perforated by electrical discharge treatment using an electrical discharge device ("GOM 690D", a product of Gakken Co., Ltd.), and peeled off from the base paper. The resulting stencil was set on a rotary printing press ("EP300", a product of Seiki Kogyo K.K.) and printing was conducted using an oily ink at a speed of 50 copies/min. 3,000 copies were printed over 3 hours, while checking the printing ink resistance every 1,000 copies by allowing to stand for 60 minutes in contact with a printing ink.

The film for use as a stencil in mimeograph printing obtained was evaluated for uniform thickness, generation of gas having unpleasant odor, uniform perforations and sharpness of prints.

The results obtained are shown in the Table below.

EXAMPLE 2

A film for use as a stencil in mimeograph printing was prepared in the same manner as in Example 1 except that γ -aminopropyltriethoxysilane ("A-1100", a product of Nippon Unicar Co., Ltd.) was used in place of N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane.

The results obtained are shown in the Table below.

EXAMPLE 3

A film for use as a stencil in mimeograph printing was prepared in the same manner as in Example 1 except that a resin having a density of 0.903 g/cm³ ("Mitsubishi Norbrene FY3", a product of Mitsubishi Petrochemical Co., Ltd.) was used as the crystalline propylene homopolymer.

The results obtained are shown in the Table below.

EXAMPLE 4

A film for use as a stencil in mimeograph printing was prepared in the same manner as in Example 1 except that the amount of N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane was changed to 0.3 part.

EXAMPLE 5

A film for use as a stencil in mimeograph printing was prepared in the same manner as in Example 4 except that the proportions of the crystalline propylene homopolymer and the acetylene black were changed to 75% and 25%, respectively.

The results obtained are shown in the Table below.

EXAMPLE 6

A film for use as a stencil in mimeograph printing was prepared in the same manner as in Example 1 except that a propylene-ethylene copolymer having a density of 0.902 g/cm³ and an ethylene content of 2.5% ("Mitsubishi Norbrene FW3", a product of Mitsubishi Petrochemical Co., Ltd.) was used in place of the crystalline propylene homopolymer.

The results obtained are shown in the Table below.

EXAMPLE 7

A film for use as a stencil in mimeograph printing was prepared in the same manner as in Example 1 except that paraffinic processing oil - ("PW-90", a product of Idemitsu Kosan Co., Ltd.) was added to the composition in an amount 5 parts by weight per 100 parts by weight of the crystalline propylene homopolymer.

COMPARATIVE EXAMPLE 1

A film was prepared in the same manner as in Example 1 except that N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane was not used.

The results obtained are shown in the Table below.

COMPARATIVE EXAMPLE 2

A commercially available film for use as a stencil in mimeograph printing made of polyvinyl chloride resin was subjected to perforation and mimeograph printing in the same manner as in Example 1.

The results obtained are shown in the Table below.

TABLE

	Thickness Distribution (μm)	Perforating Properties			Sharpness of Printing		
		Generation of Gas Having Unpleasant Odor	Uniformity of perforations		1,000	2,000	3,000
					Copies	Copies	Copies
Example 1	17-22	None	Uniform		A	A	A
"	18-22	"	"		A	A	A
"	17-22	"	"		A	A	A
"	18-22	"	"		A	A	A
"	18-22	"	"		A	A	A
"	18-22	"	"		B	-	-
"	18-22	"	"		A	A	A
Comparative Example 1	12-29	"	Non- uniform		C	C	C
"	19-22	Generated	Non- uniform		A	A	A

A: Uniform and clear

B: Unclear portions due to formation of wrinkles

C: Unclear and ununiform

The film according to the present invention for use as a stencil in mimeograph printing does not generate gas having unpleasant odor during perforation, has excellent ink solvent resistance, and has uniform perforation properties.

Claims

1. A film for use as a stencil in mimeograph printing and prepared from a composition comprising polypropylene resin and carbon black, characterised in that the composition comprises from 70 to 90% by weight of polypropylene resin, from 30 to 10% by weight of an electroconductive carbon black and from 0.05 to 3 parts by weight, per 100 parts by weight of the total amount of the polypropylene resin and electroconductive carbon black, of an organofunctional compound selected from organofunctional silanes, organofunctional titanates and organofunctional aluminates.

2. A film as claimed in Claim 1, wherein the polypropylene resin is a crystalline propylene homopolymer.

3. A film as claimed in Claim 2, wherein the crystalline propylene homopolymer has a density of at least 0.903 g/cm³.

4. A film as claimed in any preceding claim, wherein the organofunctional compound is an organofunctional silane.

5. A film as claimed in Claim 4, wherein the organofunctional silane is a compound selected from γ -aminopropyltriethoxysilane, γ -aminodithiopropyltriethoxysilane, N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane and N-bis(β -hydroxyethyl)- γ -aminopropyltriethoxysilane.

6. A film as claimed in any preceding claim, wherein the amount of the polypropylene resin is from 75 to 85% by weight and the amount of the electroconductive carbon black is from 25 to 15% by weight.

7. A film as claimed in any preceding claim, wherein the amount of the organofunctional compound is from 0.1 to 1.5 parts by weight per 100 parts by weight of the total amount of the polypropylene resin and electroconductive carbon black.

8. A film as claimed in any preceding claim, wherein the composition further includes a softening agent in an amount of from 0.1 to 25 parts by weight per 100 parts by weight of the polypropylene resin.

9. A film as claimed in Claim 8, wherein the softening agent is a paraffinic, naphthenic or aromatic processing oil.

10. A film as claimed in any preceding claim, wherein the film has a thickness of from 10 to 30 μ m.

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