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(54) **Electrophotographic sheet material and process for its preparation.**

(57) The present invention relates to an electrophotographic sheet material suitable for use as an offset printing master, which comprises a cellulosic base material having an electrical resistivity not exceeding about 10^{13} ohms/sq.cm, a continuous film of cellulose nitrate on said base material, a photoconductive layer on the surface of said film remote from the interface between said base material and said film; and to a process for the preparation of the sheet material.

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DESCRIPTION

"ELECTROPHOTOGRAPHIC SHEET MATERIAL"

The present invention relates to electrophotographic sheet material. More particularly, this invention relates to improved electrophotographic sheet material
5 suitable for use as an offset printing master.

Electrophotographic sheet material generally comprises a base sheet, for example paper, having thereon a light-sensitive coating, e.g. one containing a photo-conductive particulate material to an insulating binder.
10 Typical of such coatings are those containing zinc oxide in a suitable resin binder, such as polyvinylacetate or modified polyvinylacetate. An electrostatic image may be formed on such sheet by exposure to light projected from an original, and a visible image may then be developed
15 and fixed. The sheet with the visible image so formed may then in turn serve as a master plate for offset printing. When used in such capacity, the sheet is treated with an aqueous solution designed to render the non-imaged areas of the sheet hydrophilic (or oleophobic)
20 before running it on the offset press. Conventional sheets tend to be deleteriously affected by such treatment, as could only be expected, notably in that they quickly stretch and crease due to contact with the fountain solution on the press, become weak or delaminate and so on.
25 This limits the number of copies that can be printed with a single conventional master and with a simple conventional master it would be rare to print more than about 1000 copies.

Improvements have been proposed to make such offset
30 printing masters more durable. Canadian patent 874,905 proposes to apply on a paper base a sizing layer containing a major amount of dialdehyde starch in addition to the usual sizing agents, such as carboxymethyl cellulose, gelatin and the like, and to apply the photosensitive
35 coating on said sizing layers.

Canadian patent 862,679 proposes an electro-
photographic material having an electroconductive back
layer, e.g. of a cationic latex and an interlayer made
of vinyl polymer and amino resins. These expedients
5 however are either not particularly effective or are very
cumbersome and expensive. For example, applying the
vinyl polymer and amino resins to paper and curing at a
temperature of about 150°C represents a complex and
delicate task. Yet another proposal (Canadian patent
10 957,540) is to apply a resin coating, more particularly a
cellulose ester coating, to the back of the paper but
the results permit only up to 300 copies to be printed.

The present invention provides an electrophoto-
graphic printing sheet which can be produced in a simple
15 manner and can serve as a master plate for consistently
running off impressions on the order of up to five thousand
or more using a conventional offset base paper. Accordingly
the present invention relates to an electrophotographic
sheet material for use as a master in offset printing and
20 comprises a cellulosic base material, a continuous film
of cellulose nitrate on said base material, and a photo-
conductive layer on said film.

The cellulosic base material is preferably paper
or a like cellulose fibrous sheet material of suitable
25 characteristics. Among the characteristics expected of
such paper, an important one is electrical resistivity
which is controlled within specified limits. The proper
resistivity may be, and is generally, imparted into the
paper in a known manner, in the course of fabrication,
30 e.g. by incorporating additives in the paper body or in
the sizing. The paper may, and will generally, be sized
in a conventional manner and special ingredients may be
incorporated in the sizing to make the paper less absorbent
to water or solvents as exemplified by the above mentioned
35 incorporation of dialdehyde starch. But unsized papers
can also be used, particularly very dense and highly

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bonded papers, i.e. papers which in lieu of surface sizing have been lightly calendered to increase resistance to water and solvent penetration. Suitable grades of paper for the making of offset plates, are, for example, 5 Allied Grade X904 or Glatfelter DTMB or LTMP Grades of offset base paper (made respectively by the Allied Paper Company and the Glatfelter Company) but other base materials having the characteristics mentioned above may be used.

10 The photoconductive layer, which will form the top coating of the sheet material may be, and is normally, a dispersion of photoconductive zinc oxide in a resin system, but other similar materials may be used to form the photoconductive layer. The zinc oxide layer may be, and 15 is generally, applied as a dispersion of zinc oxide in a resin solution, the solvent being generally an organic non-polar compound, preferably a hydrocarbon for example toluene. The art of forming and applying the photoconductive zinc oxide layer is highly specialized and 20 often relies on an accumulated know-how and skills, however, it is not part of the present invention.

The cellulose nitrate film is applied on the fibrous base material to form an intermediate layer between the base and the photoconductive layer. The film may be 25 applied for example in the form of a solution of cellulose nitrate in a solvent which evaporates rapidly, e.g. an alcohol, an ether-alcohol mixture or a glycol ether. Various types of cellulose nitrate are available in commerce, differing from one another for example in viscosity (at 30 given concentration) and nitrogen content. Examples are the nitrocellulose products sold by the Hercules Company under the trademarks RS, AS and SS Nitro-cellulose. Solutions of a wide range of viscosity and/or solids content may be used. The viscosity will be chosen on the 35 basis of ease of application with given equipment and, using Meyer rods of suitable dimension, we have found the range of viscosities from about 50 to about 1,000 cps to

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be suitable. The solids content must be such that, upon evaporation of the solvent, a continuous cellulose nitrate film is formed on the base material. We have found the range of between about 1/2 lb to 6 lbs (0.23 to 2.72 kilograms) of cellulose nitrate per ream (3,300 sq ft or 39.6 square metres), of paper to be suitable, depending for example on the surface and the absorptivity of the paper; for example, the higher the absorptivity of a paper base the greater the amount of cellulose nitrate which has to be used to ensure the formation of a continuous film. The cellulose nitrate coat weight must not be too much higher than the 6 lbs. (2.72 kilograms) mentioned above, since it may adversely affect curl, electrical properties, stiffness and for flexibility of the base plate; whereas, if it is too low i.e. if it is much less than the 1/2 lb (0.23 kilogram) referred to above it may not be durable enough.

One of the requirements with regard to an electro-photographic paper base is that its electro-conductive properties be such as to permit a sufficiently rapid dissipation of electrostatic charges after exposure to light of the photosensitive layer. Such resistivity should not, in any case, exceed about 10^{13} ohms/sq cm., and since the addition of a cellulose nitrate precoat does not substantially modify the resistivity of the base paper over a relative humidity range of about 10 to 80%, it is a material uniquely suited for the purpose herein described.

The resistance of cellulose nitrate to organic aromatic solvents, such as are generally used in zinc oxide-resin dispersion make it further suitable as a barrier layer between the base paper and the photoconductive layer during the zinc oxide coating operation. Additionally, the cellulose nitrate improves the water holdout and dimensional stability of the base sheet which contributes significantly to obtaining improved press run capacity.

Care should be taken not to cause the thus pre-coated base paper to acquire a curl and in certain cases, it may be necessary to employ compatible conventional techniques to avoid curl.

5 The invention will be further illustrated by means of the following Examples:

Example 1:

Cellulose nitrate, sold under the name RS Nitrocellulose (Hercules Trademark) 1/4 sec., was dissolved
10 in glycol ether sold in the trade as CELLOSOLVE (Union Carbide trademark) in the proportion of 14 gm cellulose nitrate and 86 gm CELLOSOLVE (TM). The thus prepared solution was applied by Meyer bar coating methods onto Allied Grade X904, 78 lb (3.54 kilograms) offset base
15 paper. The solvent was allowed to evaporate and the resulting continuous film of cellulose nitrate amounted to about two pounds (0.91 kilograms) per ream (3,300 sq. ft. or 39.6 square metres) of paper. The thus pre-coated paper was then used as a substrate for a conventional zinc oxide coating applied at a weight of about
20 22 lbs (9.98 kilograms) per ream (3,300 sq. ft. or 39.6 square metres). The electrophotographic paper thus produced, when imaged and toner developed, was used as a plate in an offset press. The number of impressions
25 obtained with each plate was always in excess of 5000. When the same paper was used, without pre-coating with cellulose nitrate, as a substrate for a zinc oxide photosensitive coating, the resulting electrophotographic plates run in a similar manner in an offset press,
30 produced only 500-1000 impressions.

Example 2.

A solution similar to the one in Example 1 was prepared consisting of cellulose nitrate sold under the name SS Nitrocellulose (TM) 1/2 sec. in ethyl alcohol in
35 the proportion of 10 gm solvent. The formulation was applied onto a paper in the same manner as the preceding Example to form a film of a weight of about 3 lbs (1.36

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kilograms) per ream (3,300 sq. ft. or 39.6 square metres). A zinc oxide photoconductive coating of a weight of 20 lbs. (9.07 kilograms) per ream (3,300 sq.ft or 39.6 square metres) was applied onto the thus pre-coated paper. Plates prepared from this electrophotographic paper were used on a conventional offset press and about 5000 impressions were produced with only minimal stretch (about 0.2%) of the offset plate in both the machine and cross-machine directions. A zinc oxide coated identical paper base, but without the intermediate film of cellulose nitrate stretched about 0.4% in the machine direction and about 2% in the cross machine direction after about 1000 impressions.

Example 3:

A paper base having a high solvent holdout and sold as E.B. Eddy Silicone Coating base (TM) by the E.B. Eddy Company was coated on both sides with a solution of RS Nitrocellulose (TM) and having 1/2 second viscosity, was dissolved in CELLOSOLVE (TM) in the proportion 10 g. of nitrate to 90 g of solvent. This solution, when applied to the paper and dried, provided a pre-coating of 2 lb (0.91 kilograms) per ream (3,300 sq.ft. or 39.6 square metres) of substrate. An overcoat of 22 lb. (9.98 kilograms) per ream (3,300 sq.ft. or 39.6 square metres) of zinc oxide was applied to the precoated substrate. The substrate, so-coated, when imaged, developed, converted and run in an offset press as the offset plate provided about 1,000 impressions per plate. A similar base material with the zinc oxide overcoat, but without the cellulose nitrate coating provided about 50 impressions per plate.

The description and examples provided above are for the purpose of providing a complete disclosure of the invention, and alterations and modifications within the scope of the appended claims, may occur to those skilled in the art.

CLAIMS.

- 5 1. An electrophotographic sheet material characterised in that it comprises a cellulosic base material having an electrical resistivity not exceeding about 10^{13} ohms/sq.cm, a continuous film of cellulose nitrate on said base material, a photoconductive layer on the surface of said film remote from the interface between said base material and said film.
- 10 2. Electrophotographic sheet material according to claim 1, characterised in that said base material is an offset base paper.
- 15 3. Electrophotographic sheet material according to claim 2, characterised in that said continuous film of cellulose nitrate constitutes between 1/2 to 6 lb. (0.23 to 2.72 kilograms) per ream (3,300 sq. ft. or 39.6 square meters) of said sheet material.
- 20 4. Electrophotographic sheet material according to claim 1, 2 or 3 characterised in that said photoconductive layer contains zinc oxide.
- 25 5. Process for the preparation of electrophotographic sheet material characterised by the steps of coating a cellulosic base material having an electrical resistivity not exceeding about 10^{13} ohms/sq. cm. with a solution of cellulose nitrate, removing solvent from said solution on said base material thereby to form a continuous film of said cellulose nitrate and coating a layer of photoconductive material on said continuous film of cellulose nitrate.
- 30 6. Process according to claim 5, characterised in that the base material is an offset base paper.